ASSESSMENT OF ANAEROBIC TREATMENT OF SELECT WASTE STREAMS IN PAPER MANUFACTURING OPERATIONS

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ASSESSMENT OF ANAEROBIC TREATMENT OF SELECT WASTE STREAMS IN PAPER MANUFACTURING OPERATIONS

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I dedicate this Thesis to

my father, Mario Szeinbaum,

for being a constant source of inspiration

in the effort of always giving the best of oneself.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

SUMMARY

The most common strategy for handling paper mill solid waste is typically disposal in landfills. Several drawbacks, however, are associated with this type of solid waste management, such as increasing costs due to oil price rise, governmental restrictions on land use, and environmental concerns such as leaching of disposed contaminants into groundwater, as well as methane generation of and release to the atmosphere, which contributes to global warming. An alternative to reduce solids prior to disposal and to recover methane as a renewable fuel is anaerobic digestion, but it is not yet clear whether such an approach is feasible in paper mills.

In this study, the anaerobic digestion of paper mill waste streams was evaluated for a paper plant located in Central America, to assess to what extent certain waste streams can be anaerobically digested, to what extent energy can be produced in the form of methane for implementation in a wastewater treatment plant, and to evaluate the conditions that will favor methane generation from select waste streams.

Batch assays were performed to evaluate the biodegradability of single and combined waste samples under ideal, laboratory conditions. Samples were obtained from the manufacturing plant as well as the wastewater treatment plant at the paper mill under study. The ultimate biodegradability ranged 25 to 85% in terms of volatile solids destruction, corresponding to the waste activated sludge (WAS) and Flotation Cell rejects, respectively. The chemical oxygen demand (COD) destruction of single samples ranged from 45 to 63%, corresponding to WAS and wastewater treatment plant (WWTP)

dissolved air flotation (DAF) skimmings, respectively. Methane generation ranged from 80 to 190 ml at 35^{o}C/g COD added for all single samples (excluding underflows). In combination Feed 1 was reduced by 46 and 52% and Feed 2 by 27 and 38%, respectively.

Two combinations of two single samples each (Feed 1 and 2), formulated according to plant operational data and the results obtained in the batch assays in terms of their solids and COD destruction , were evaluated at different solids retention times (30, 20, 15, and 7 days) in semicontinuous flow anaerobic digesters. Nutrients (N, and P) availability as well as alkalinity in the plant waste streams were evaluated and minimum supplements were used to support an efficient anaerobic digestion process. The reactors reached stable operation at all retention times evaluated. Methanogenesis was the predominant, terminal metabolic process under anaerobic, mesophilic conditions, but the overall process rate was determined by the hydrolysis of the particulate substrate. Reactors fed with Feed 1 achieved the highest level of destruction, which amounted to 85% of the biodegradable portion of volatile solids at a solids retention time of 20 days. The methane yield varied from 94 to 120 ml of methane at 35^{o}C per gram COD consumed. Nutrient (N and P) availability had the largest impact on the performance of the reactors, given the very limited amount of nitrogen and phosphorus that is typically present in paper mill wastes. Alkalinity addition to the feed (3.5 mg $NaHCO_3$/L) was necessary to maintain the reactors pH above 6.9.

The results of this study demonstrate that anaerobic digestion of select paper mill waste streams is a feasible alternative leading to a decrease of landfill disposal of solid wastes, as well as the production of energy in the form of methane, and sets the basis for further evaluation of the full potential of this process in paper mills, especially in Latin America.

CHAPTER 1

INTRODUCTION

Papermaking is known to be a water intensive process. To reduce water consumption, water recycling is employed, where a portion of the fibers are also reclaimed (de Alda 2008). Even though wastewater generation is greatly reduced, the resulting wastewater has high COD values and solids, which are typically mechanically separated before the wastewater enters the secondary treatment units. The resulting primary sludge is disposed of in landfills, together with secondary sludge from the biological treatment. Paper mill primary sludge contains wood fibers as the principal organic component, and inorganic materials such as kaolin, $CaCO_3$, TiO_2, etc., that are used as paper fillers (de Alda 2008).

As landfill costs are rising because of regulations, space becoming more expensive and transportation costs rise, alternatives to current waste solids disposal management are needed. An alternative method of reducing solids is anaerobic digestion, where a mixed culture of fermentative and methanogenic microorganisms utilize this waste as their carbon and energy source. Not only the volume of solids can be reduced, but as methane is released in the process and can be utilized (e.g., for steam and/or electricity production), anaerobic digestion has the potential to add value to the waste.

In the papermaking industry the process variability, the type of paper produced, and the primary products used is so large that different paper mills may discharge effluents with significantly different composition (de Alda 2008; Kumar et al. 2008). It is therefore important to rationally design a treatment process that specifically targets the

characteristics of a specific paper plant, in order to apply appropriate technology and proper disposal of wastes.

In this study, the anaerobic digestion of paper mill waste steams was evaluated in a plant located in Central America, with the objective of determining the feasibility of this type of treatment method to reduce solids prior to disposal and generate methane. This plant produces tissue paper products using only post-consumer recycled fibers, and is one of many Latin American and Caribbean plants that currently operate in this mode. Such plants could potentially implement the proposed technology.

The specific objectives of this study were:

1) To investigate whether certain waste streams can be anaerobically digested to reduce the amount of solids to dispose of and which ones can be potentially implemented.

2) To assess the potential solids reduction and energy production in the form of methane for implementation in a wastewater treatment plant.

3) To evaluate the conditions which favor methane generation from select paper mill waste streams.

CHAPTER 2

BACKGROUND

2.1 Paper Mill Waste Generation and Management

2.1.1 Paper Mill Waste Origin and Composition

Fibers for paper production (pulp) can be obtained from wood, agricultural crops such flax, rice and wheat straw, as well as from recovered paper. During the production of paper products, solid wastes (sludge) are generated, which can be of different origin: the wastepaper coming from the production of virgin wood fiber, the wastepaper produced by removing ink from post-consumer fiber (de-inking paper sludge), or the activated sludge from the secondary treatment systems (secondary sludge) (Beauchamp et al. 2002).

Traditionally, wastes from the paper industry contained residues from both pulping and paper making processes. Originally, paper products were obtained from virgin pulp by mechanically and/or chemically separating it from the rest of the plant materials. In the last decades, however, due to the increased consumption of paper products and the increasing awareness of the environmental impact of pulping, many mills have included secondary pulp (from recycled paper products) in their final products. The percentage of plants including some proportion of recycled fibers has now reached a recent value of at least 78% of the existing mills in America, as of 2005 (Huang and Logan 2008) . Some

paper mills, such as the system considered in the present study, employ 100% of recovered paper in their products.

Since many paper mills rely on reusing paper, the pulp industry and the paper industry are sometimes separate industries, and the processes and chemicals used in the pulping and the papermaking operations are very different. As a result, wastewater from the papermaking and de-inking process also differs significantly (Thompson et al. 2001).

Therefore, considering that waste composition and characteristics have changed, it is important to review the current treatment alternatives employed and reconsider those that have been overlooked because they were not suitable in the past. The composition of the waste paper is the principal parameter that needs to be considered, although this is not easy to determine, as a variety of industries provide post-consumer paper to reuse in a mill, ranging from office waste paper to waste packaging paper. This results in the generation of an undetermined mixture of wastes. However, recyclable paper does have general characteristics that allow it to be reused. A brief description of what is expected to be found in the wastes of a typical paper mill is provided below along with the potential implications to the waste treatment process and their discharge into the environment.

Cellulose and Hemicellulose. Cellulose fines and other additives can be up to 50% of the total mass of the whitewaters produced. Cellulose is composed of building units called cellobiose, two glucose molecules joined by a β-1,4 glycosidic bond (Bayer *et al.* 1998). Complete hydrolysis of cellulose yields glucose, an easily biodegradable carbon source. This component can contribute to an excessive BOD load in receiving water bodies as part of the untreated paper mill effluent (highly charged whitewaters), but when a

secondary treatment is employed, cellulose can be mineralized. Hemicelluloses are relatively low-molecular weight, branched heteropolysaccharides associated with both cellulose and lignin and together build the plant cell wall material (Bayer *et al.* 2006). Apart from cellulose and hemicellulose, additives are used during the papermaking process. A variety of chemicals will confer different properties on the paper sheet, such as sizing agents, fillers to improve the scattering coefficient (opacity) and reduce ink absorbency, such as clays and other minerals, or color and other aesthetic properties, modified with dyes. Also, since all wood cellulose fibers get negatively charged when they are extracted from the primary substrate, as many additives also do, the addition of cations such as aluminium, in the form of $Al_2(SO_4)_3$, is employed to promote bridging between fibers, thus improving the retention of fines. Addition of these chemicals not only increases the amount of organic/inorganic solids that need to be treated, but when employing secondary treatment, they may be toxic to the biota and therefore decrease the efficiency of the treatment processes (Walker 2006). Chemicals typically used in papermaking are described below:

Biocides. These chemicals are added to protect machinery and paper produced from microbial growth, which is frequently a problem. This occurs because the process deals with a high concentration of easily biodegradable substances such as hemicelluloses, particularly when water is recirculated to reduce water consumption, and is also facilitated by the high operation temperature during paper manufacturing. Wide range spectrum biocides are typically used, which may also affect the viability of necessary microorganisms such as those in the secondary wastewater treatment units, or affect biota in the receiving water bodies if not biodegraded. Typically, biocides consist of oxidizing

agents (hydrogen peroxide), or organic chemicals (e.g., organo-thiocyanates, organo-bromo compounds).

Surfactants. These chemicals are typically added to avoid biofilm formation as well as cleaning agents, antifoamers, deinkers, dispersants, and for other purposes. These chemicals are also detrimental to secondary wastewater treatment microbiota, as well as having environmental toxic impacts on natural macrobiota. Typical surfactants include alkylbenzene sulfonates and alkylphenol ethoxylates.

Fillers. Fillers include inorganics such as clay, calcium carbonate, as well as color pigments. These additives are mostly the inorganic constituents of waste.

Adhesives. Usually, only post-consumer paper with very low percentage of adhesives (around 2% w/w) is selected for recycling. However, as a result of water reuse, these organics may accumulate over time.

Inks. Inks are a component of recycled paper. Therefore, as the proportion of recycled paper increases, so does the amount of inks present in the manufacturing system. However, the final product needs to be free of ink, and therefore de-inking is an important, although complex, step. Washing and flotation processes are used to remove printing inks, and are employed in the plant considered by the present study. Historically, inks were hazardous to the environment, but their heavy metal content is now reduced to acceptable limits (Jacob et al. 2005).

Regarding the environmental impact of wastes from paper mills, not having the pulping process may be considered an advantage for these manufacturing plants, as the amount of potentially toxic chemicals that need to be treated is significantly less, which alleviates the need for advanced treatment and the potential for secondary treatment upsets due to

the presence of toxic substances. For example, in recycled paper effluents, the amount of lignin, which is toxic to the methanogens is very low (Yin 2000). Also, importantly, the amount of wood extractives (sterols, lignans) is expected to be very low. These chemicals are released during the pulping processes to obtain cellulose from biomass and, when dissolved in water, may result in toxicity in the secondary wastewater treatment or in the receiving water bodies (Lacorte et al. 2003). Given that wood-free waste paper is used for tissue production, wood extractives are unlikely to be a problem in tissue production.

To sum up, the portion and quality of fibers and additives depend on the type of paper that is produced, and are as varied as the existent classes of paper. Given that a plant may obtain their fiber from reclaimed paper of different sources, the exact chemical composition of the paper mill waste streams is usually unknown, and probably unique, or significantly different from that of another paper mill (Kumar *et al.* 2008; Kuokkanen *et al.* 2008; Latorre *et al.* 2007). As a result, different levels and strength of organic wastes are generated and need to be treated, or potential toxicity in the secondary wastewater treatment may vary considerably. Therefore, although some general characteristics can be assumed, the treatment options and conditions are expected to need to be tailored to a particular scheme of production.

2.2 Treatment of Paper Mill Wastes

2.2.1 Treatment Options of Wastewater

The papermaking industry is one of the largest water users and generates large quantities of highly polluted wastewater. In the last decades, the organic loading in paper mill waters has increased. Because of environmental and legislative pressure as well as by technological advances, water reuse has become a common procedure to reduce water consumption which has been reduced by 80-90% (Asghar *et al.* 2008; Lerner *et al.* 2007; Thompson *et al.* 2001). With each recycling cycle, the fibers in the paper become shorter and the acceptable use is more restricted. As a result, a normal cycle produces white bond paper, then colored bond paper, newspaper, grocery bags, and finally toilet paper. The reuse of water not only causes several problems in the manufacturing operations, such as build up of slime (undesired growth of microorganisms), but also, most importantly, white waters get highly charged with organic matter as well as inorganic paper constituents (Ali and Sreekrishnan 2001; Lacorte *et al.* 2003; Lerner *et al.* 2007; Thompson *et al.* 2001).

Many paper mills treat their wastewaters by a primary treatment, followed by some form of secondary treatment (Atkinson *et al.* 1997; Latorre *et al.* 2007; Thompson *et al.* 2001). Since the wastewater is high in solids and COD, a primary treatment is needed to separate the solids from deinking, recycling of whitewaters, or from the waste activated sludge. Solids separation may be done by sedimentation or flotation in order to remove cellulosic fibers, lignin and sand from the effluent (Rittmann and McCarty 2001; Stoica *et al.* 2009; Thompson *et al.* 2001). The solids are further dewatered and typically disposed of in landfills or incinerated (Beauchamp et al. 2002; Zule et al. 2007). Solids incineration is usually not the preferred alternative because, even upon dewatering, these wastes have high water content, of at least 50% (Stoica *et al.* 2009).

Secondary wastewater treatment typically involves an aerobic activated sludge step, followed by clarification and release of the effluent to a water body. Other treatment options, such as membrane filtration are available, but usually costs associated with these technologies limit their application (Thompson et al. 2001). Anaerobic treatment, although common for agricultural and municipal wastes, is not common in the pulp and paper industry (Thompson et al. 2001).However, it is noteworthy that as paper waste composition is changing over time, the application of anaerobic treatment of wastewaters or anaerobic digestion of solids might become a more common, and sustainable alternative.

2.2.2 Drawbacks Associated with the Current Solid Waste Management System

2.2.2.1 Disposal Costs

In order to dispose of the solids generated in the papermaking and the wastewater treatment processes, solids are pressed or centrifuged to reduce the amount of water, and then transported by truck to their final destination in which they are disposed. Transport and disposal account for a large portion of the total waste treatment costs (around 75% in the system considered in this study). This is partly because, even after flotation and drying, solids still have a high water content (Levy and Taylor 2003; Thompson *et al.* 2001). Considering that oil price is increasing over time (DOE 2008), and that regulations on carbon emissions and land use are getting more stringent, it is foreseen that disposal costs will inevitably rise (Levy and Taylor 2003). Furthermore, if it is taken into account

that biomass is a potential source of energy as methane (or biogas), which can be generated by anaerobic digestion, not utilizing it as such can be considered as a cost to the industry that generates it.

2.2.2.2 Environmental Impact of Solid Waste Disposal

Methane is produced in landfills because anaerobic conditions are created as waste is disposed of with the appropriate amount of moisture content. Municipal waste landfills are the largest anthropogenic source of methane in the U.S.A., accounting for 34% of all methane emissions (Kumar et al. 2004). Methane is 23 times more potent than carbon dioxide as a greenhouse gas, and under normal conditions, being lighter than air, it is lost into the atmosphere (DOE 2004). Therefore, the uncontrolled release of methane from landfills is an important environmental problem. The possibility of engineering a system to obtain methane from solid wastes not only reduces the environmental impact of the uncontrolled release of a potent greenhouse gas, but also makes the solid wastes a significant renewable energy resource.

2.2.2.2 Additional Requirements of the Aerobic Secondary Treatment of Paper Mill Wastes

Because of the nature of the wastes (high in carbon content but very low in nitrogen and phosphorus), nutrients need to be supplemented. This is a concern not only because the right dose needs to be achieved in order to obtain a stable system without leaving these nutrients in the final, treated effluent, but also because nutrient addition increases the treatment cost. Also, the system is highly dependent on the well functioning of aerators, which consume large amounts of energy. Furthermore, when the plant is in continuous

operation, it is difficult to clean or repair when it is needed, and climatic conditions of usually high temperature (around 30˚C) in Central America make this a common problem. Also, maintaining a proper control of the dissolved oxygen (DO) concentration in the aeration tank and maintaining a good settling sludge are not easy. Settling of activated sludge treating paper mill wastewaters seems to be particularly prone to being very variable as filamentous bacteria dominate in these reactors, and often create conditions of bulking in the clarifier (Thompson et al. 2001).

2.3 Alternative Treatment Option: Anaerobic Digestion of Paper Mill Wastes

2.3.1 Methane Generation in Anaerobic Digestion of Industrial Wastes

The anaerobic treatment of wastes has many potential benefits, and several industries have widely adopted this type of treatment. Many municipal wastewater sludges and solid wastes in the U.S. are being treated this way, and the process has been found to be fairly reliable (Rittmann and McCarty 2001). In agricultural systems, anaerobic digestion has been successfully applied. In many cases, biogas is used to generate electric power, with many of the farms recovering waste heat from the electricity generating equipment for on-farm use (generating about 244,000 MWh of electricity per year in a typical US farm) or use of the gas in boilers, for example. As of February 2009, the combustion of biogas from agricultural digesters prevented the emission of about 36,000 metric tons of methane annually, plus the amount of greenhouse gases saved from the use of fossil fuels, in the US (EPA 2009).

2.3.3 Generation of Methane and its Value

Methane generation from biomass has its inherent value. As opposed to the mineralization of the organic matter to CO_2 that results from an aerobic treatment, which is subsequently released into the atmosphere and contributes to the overall pool of greenhouse gases, in the anaerobic treatment of organic solids, methane is generated, which can be collected and utilized as a fuel. Therefore, even though the final product will be CO_2, the biomass is not completely unutilized.

Methane yields 890 KJ/mol or 380,000 BTU/m^3 when burned with oxygen (Insam and Wett 2008). Methane is flammable at a ratio of 5-12% of CH_4 in air, so with typical, expected biogas content of around 50% of methane, anaerobic digestion of wastes is a good alternative to generate useful biogas. Furthermore, when employing waste biomass, the generation of methane is considered a renewable source of fuel production, which adds value to the waste, as opposed to viewing it as a cost. Also, in terms of safety, since the gas density relative to air is 0.55, in case of leaks it will migrate to upper spaces, and not become a hazard (Noyola et al. 2006).

Lastly, methane generation is and will become even more important in the near future, not only because prices in fossil fuels continue to rise and alternative energy sources will need to be used, but also because the natural gas price is continuously rising, therefore becoming more valuable over time. Figure 2.1 shows the increase in the price of natural gas since 1994.

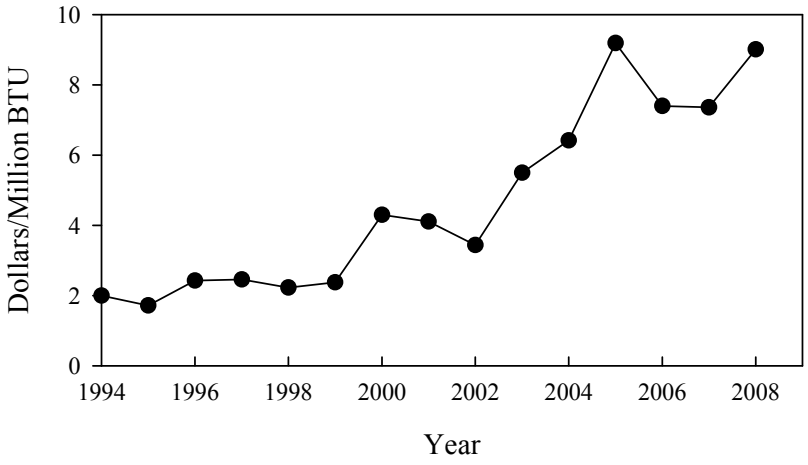

Figure2.1. Methane price vs. time in the U.S.A (DOE 2008)

2.3.2 Potential for the Anaerobic Digestion of Paper Mill Wastes

One of the advantages of anaerobic digestion is that this process can be applied to waste treatment in engineered systems when wastes are high in organic content that would be unsuitable for aerobic processes, as they would require large amounts of oxygen, impossible to be satisfied due to physical limits in the oxygen mass transfer as well as the addition of nutrient. Moreover, less biomass is generated in anaerobic treatment systems compared to aerobic systems, because microbes need to consume more energy to grow at the same rate as organisms with aerobic metabolism, and therefore a larger proportion of carbon is diverted to energy generation rather than utilized for biomass generation. Therefore, anaerobic digestion has the benefit of lowering the costs of disposal when compared to aerobic systems. In addition, as a result of lower yield coefficient, nutrient requirements, such as nitrogen and phosphorus, are also considerably less compared to aerobic treatment (Rittmann and McCarty 2001).

Finally, the use of anaerobic processes generates energy in the form of biogas (methane). Methane can be used for heating or for the generation of electrical power. Energy requirements in aerobic systems, particularly for aeration, results in them being a net energy consumer instead of a net producer, as would be the case with methanogenic systems. This is important not only because of the inherent economic benefit of utilizing this fuel in several papermaking plant processes, such as the heating of boilers for pulp drying during manufacturing, but also due to the increasing awareness and pressure from governmental and non-governmental organizations towards the decrease in emissions of greenhouse gases and the use of renewable fuels (Demirel 2008; Show and Lee 2008). In the case of the paper industry, since methane is generated by the use of biomass (i.e., biomass generated by photosynthesis), the methane generated is considered a renewable form of energy. On the other hand, disadvantages of anaerobic digestion include low microbial growth rate, particularly for methanogens (Archaea), which puts a limit on the minimum solids retention time allowed, odor production, and high buffer requirements for pH control (Rittmann and McCarty 2001).

As mentioned previously, although many industries have adopted anaerobic technology, it is still not largely used in the pulp and paper sector. This may be due to concerns relative to toxicity generated during water recycling, particularly because of the chemicals used in pulping processes, and the wastes generated from it (e.g., lignin). However, secondary fiber is mostly composed of cellulose and inorganic constituents, and is free of many recalcitrant and/or toxic compounds typically associated with pulping

operations. As the use of these types of fiber is increasing, application of anaerobic treatment may become a feasible, convenient option, which is worthy of study.

2.3.4 Biochemical Principles of Anaerobic Digestion

During the anaerobic decomposition of organic matter, gas is generated with a typical composition of 60–65% methane (CH_4) and 35–40% carbon dioxide (CO_2). Other gases might also be present, such as hydrogen sulfide (H_2S), nitrogen (N_2), hydrogen (H_2) carbon monoxide (CO) and other volatile organic compounds (VOC) (EPA 2008). These gases evolve because, during anaerobic digestion, organic materials are microbially utilized in a closed, oxygen free, reductive environment, a process that results in the transformation of organic matter into these gaseous forms.

Methanogenesis is the last one of a series of steps, of a pathway that involves several species of distinct niches, that act together to create an overall favorable reaction (Figure 2.2). The several sequences of reactions that take place during the digestion process have been well characterized. The first steps in these series are the disintegration and hydrolysis of complex, particulate matter into soluble macromolecules. Hydrolysis is achieved by bacteria that secrete enzymes into the medium (Bayer *et al.* 2006; Pavlostathis and Giraldo-Gomez 1991). In this step, soluble carbohydrates, proteins, lipids and inert material are generated. Soluble organics are either fermented or anaerobically respired and acidogenic bacteria generate volatile fatty acids, alcohols, and ammonia. During anaerobic digestion of secondary fiber, cellulose and hemicelluloses, its major constituent, are used as carbon and energy sources, and hydrolyzed to cellobiose, and further to glucose while hemicelluloses are hydrolyzed to pentoses and hexoses (Pareek et al. 2000). Organic molecules are finally converted into acetate, CO_2,

and H_2. Two types of metabolic steps finally generate methane: one mediated by hydrogenothrophic organisms, which utilize hydrogen as the electron donor and reduce carbon dioxide (electron acceptor) to produce methane (hydrogenotrophic methanogenesis; equation 2.1); the second step is mediated by acetotrophic Achaea, which utilize acetate and produce methane in a disproportionation reaction where part of the molecule receives an electron donated by the other part (acetoclastic methanogenesis; equation 2.2) (Madigan et al. 2009).

$$CO_2 + 4H_2 \Rightarrow CH_4 + 2H_2O \quad (2.1)$$

$$CH_3COO^- + H_2O \Rightarrow CH_4 + HCO_3^- \quad (2.2)$$

The final composition of the gas mixture depends on the chemical composition of the organic and inorganic matter present in the feed as well as on the physicochemical conditions of the system (pH, alkalinity, temperature). For example, anions such as sulfate and nitrate, are involved in competing processes with methanogenesis. Also, only a portion of the total COD added to a system may be anaerobically biodegradable (Batstone *et al.* 2002).

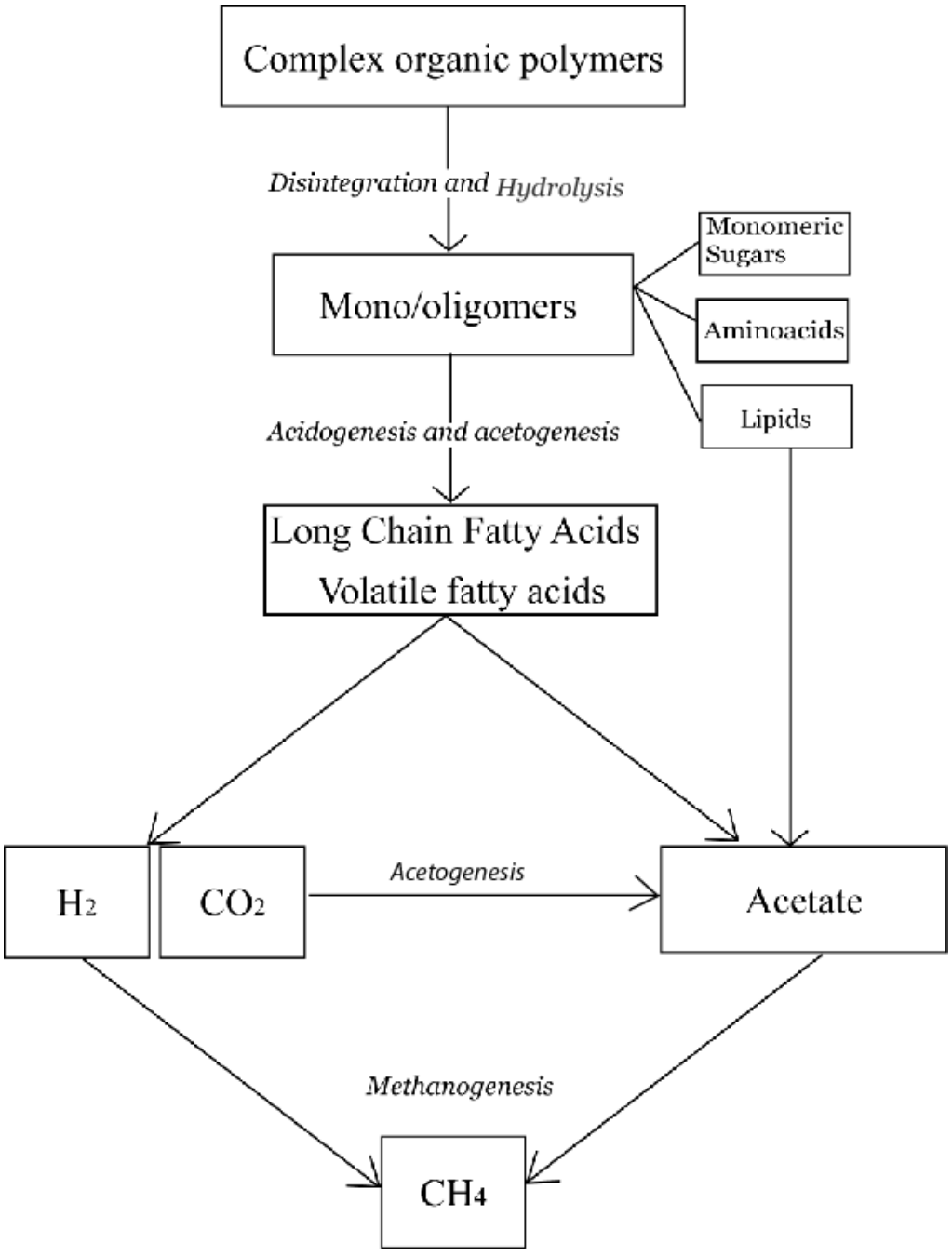

Figure 2.2. Simplified scheme of the biochemical steps that lead to methanogenesis from complex organic material. Scheme adapted from the Anaerobic Digestion Model No.1 (Batstone et al. 2002; Madigan et al. 2009).

2.3.5 Anaerobic Digestion Reactors

The composition of the microbial community plays a role in determining the performance of an anaerobic digestion system. Therefore, not only the nature of the substrates to be digested is important, but also operational and environmental parameters that influence the behavior and fate of the microbial populations will affect the performance of the anaerobic system (Demirel 2008). Key parameters include the solids retention time, which is usually not below 5 days given the slow growth rate of methanogens, organic loading rate, nutrient availability, and most importantly, an appropriate pH level, crucial for the survival of methanogens (Rittmann and McCarty 2001).

2.3.6 Feasibility of Anaerobic Digestion of Paper Mill Sludges

To sum up, as already mentioned, with respect to the applicability of anaerobic digestion of paper mill wastes, only in the past few years the pulp and paper processes have been separated into two distinct industries, resulting in the generation of different types of wastewater, and therefore a new opportunity to apply anaerobic technology has been created. However, there is not much literature available on the study and/or application of anaerobic digestion on paper mill wastes.

There are various reasons why it is important to study the application of anaerobic digestion of paper mill wastes. Firstly, since many digestion studies have been performed with pure components, such as cellulose as the only source of carbon, it is important to investigate how well a system performs with actual wastewater samples. Also, secondary

fiber wastes are highly charged in degradable organics from the reuse of water and lack raw materials and chemicals from the pulping industry, making them an attractive source for methane generation. Further, much of the pulp used for paper products comes from recycled paper, and as mentioned previously, it is to be expected that different mills will have wastewaters with unique characteristics. It is therefore important to study a variety of paper mills. The present study focused on the characteristics of paper mill waste streams from tissue manufacturing operations in a paper mill in Central America, to evaluate the potential of anaerobic digestion for the reduction of solids and methane generation.

CHAPTER 3

SYSTEM OF STUDY

3.1 Waste Generation During Paper Manufacturing Operations

In the manufacturing process of a tissue producing plant in Central America, the production includes white and "natural" tissue paper. Figure 3.1 shows the appearance of these two types of tissue. In this process, wastewater and solid waste are treated by a primary process of flotation and a secondary treatment is employed for the resulting wastewater. Figure 3.2 shows a simplified scheme of the waste generated at several points during the manufacturing and treatment processes. The waste generated in these points is explained below.

Natural and white tissue are produced in two mills, one which always operates in white, and the other one which alternates between natural and white tissue, in two week periods, on average. About 1700 million tons of tissue is produced each month (consuming 2,561,043 kWh per month). To generate the final tissue products, recycled paper is homogenized and converted into a (secondary) pulp with a combination of water from a natural spring and also from recovered water from the process. After homogenization, the pulp goes through a deinking step by flotation or addition of chemicals for the natural or white paper, respectively. Deinking by flotation is the first source of solid waste generated during the manufacturing process (Solids 1 in Figure 3.2), with an average flow rate of 49,000 gallons per day of around 50 g/L of solids.

Figure 3.1. Natural and white finished tissue rolls.

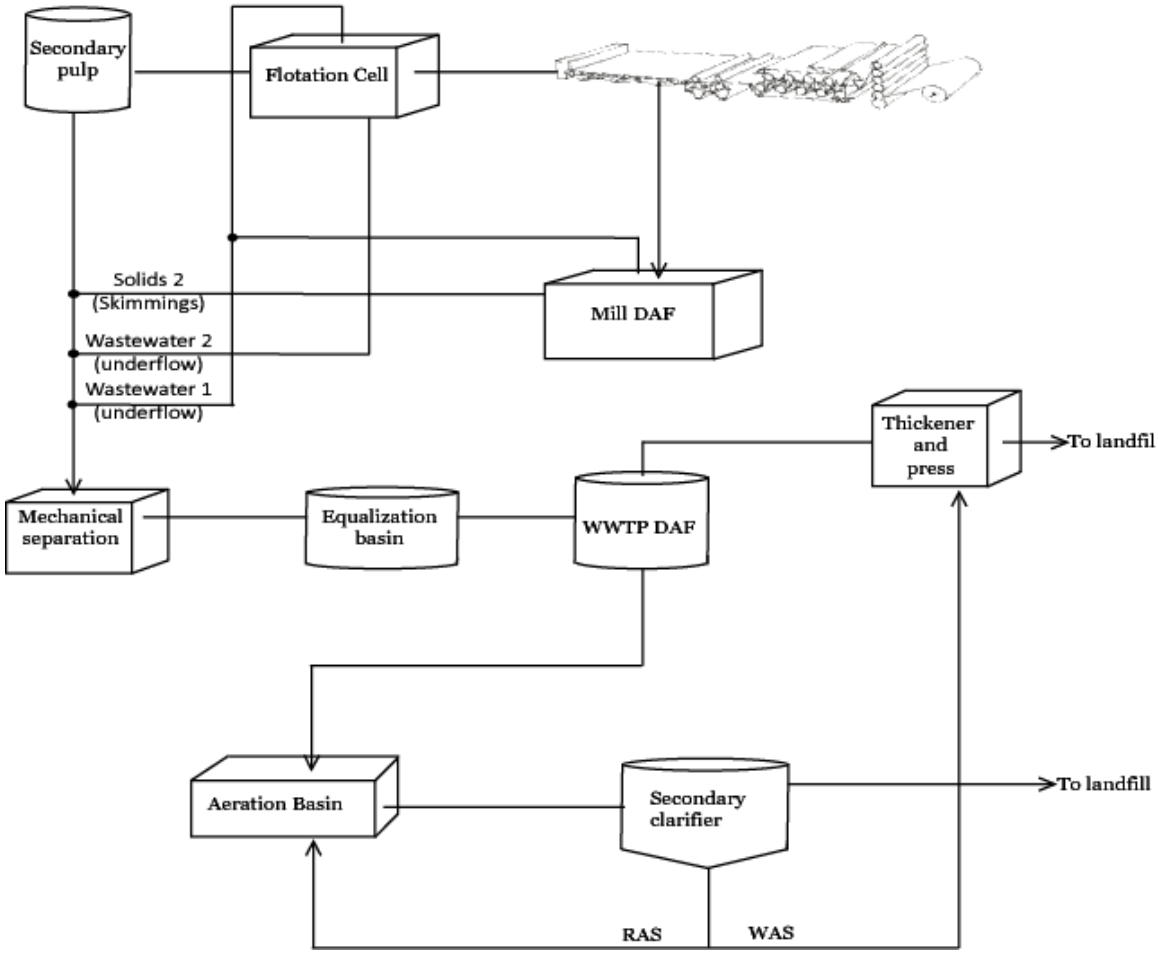

Figure 3.2. Paper making manufacturing and wastewater treatment simplified scheme. This scheme shows several steps which generate solid waste and wastewater during the manufacturing process, and the unit operations that are carried out during the primary and secondary treatment of wastes.

To form the final product, a very dilute suspension of fibers that was previously washed and screened, is deposited on a moving wire mesh screen of the paper machine. On the wire, the pulp is dewatered, but along with the water a portion of fibers is lost in each cycle. As a means to increase productivity and reduce water consumption, part of this water is recovered and recycled for pulping, as previously mentioned. In order to reuse this water, flotation is used to separate the solids for disposal. This is the second source of solids generated during the manufacturing process (Solids 2 in Figure 3.2). The fibers are left to drain and further pressed and dried on steam-heated rolls to remove all the water, which results in the formation of randomly aligned and interwoven fibers that form a layered structure held together mainly by hydrogen bonding (tissue paper).

3.2 Waste Generation During Wastewater Treatment Operations

The wastewater that reaches the treatment plant includes streams from the flotation cell and mill dissolved air flotation (DAF) skimmings and underflows. The purpose of the previous separation is to reuse part of the underflow, so the new mixture is of a different quality than the influent that enters each tank. After a first screening, the WWTP influent is equalized, and then solids are again separated by a DAF system (WWTP DAF in Figure 3.2). The skimmings generated in the WWTP DAF (Solids 3 in Figure 3.2) are then dewatered and disposed of in landfills. Currently, around 1,300 tons of solid waste is generated in the WWTP each month, with a water content of around 50%. The DAF underflow is treated by a conventional aerobic activated sludge system (Aeration tank in Figure 3.2), and the final effluent is discharged in a nearby stream, at a rate of around 600 gallons per minute, or 850,000 gallons per day. Waste activated sludge (WAS in Figure

3.2) is dewatered in combination with the DAF skimmings and then disposed of in landfills.

3.3 Proposed Changes to the System

Several waste streams are generated during the manufacturing of tissue paper, as well as in the wastewater treatment system, that are ultimately disposed of in landfills. Some of these waste streams are potentially suitable to be digested anaerobically, either singly or combined. After taking into consideration the characteristics of each waste stream, two different alternative scenarios to the current system were developed. Both scenarios consider digestion of a combination of solid waste streams. The first type of modification to the current treatment system would consist of digesting a combination of Flotation Cell Skimmings (deinking sludge) and Mill DAF skimmings. The second scenario would be to utilize the skimmings from the WWTP DAF together with the WAS. This does not modify the current operating scheme, but adds a digestion step. The resulting digested sludge would then be dewatered and disposed of as currently done in landfills. Anaerobic digestion will decrease the amount of solids generated thereby reducing the costs of disposal and the pressure on the ecosystem where the waste is disposed of. Additionally, methane gas will be produced, which can be utilized to heat water used in the process, the value of which was described in the previous chapter.

In the plant considered in the present study, and probably in several similar plants that operate in Latin America, there are many characteristics that make anaerobic digestion a

suitable technology. Firstly, the papermaking process is less toxic than if a wood pulping step was included in the process. This plant relies 100% on post-consumer paper, where wood extractives and raw materials are not present, and pulping chemicals are not used. The quality of the fibers used for tissue production is usually low, which means that they are shorter and, therefore, easier to disintegrate and hydrolyze. Finally, the process itself releases water streams that are around 65˚C and get cooler by the time they reach the wastewater treatment plant, but ambient temperature is never below 20˚C. Therefore, mesophilic anaerobic digestion should be suitable, with no need of using energy to heat the digesters.

3.4 Experimental Approach

3.4.1 Phases of Study

With the objective of reducing the amount of solids generated, and the associated potential benefit of generating useful methane gas that may be used in the papermaking process, we propose that anaerobic digestion is a treatment option that could be applied to the waste streams generated in the papermaking process of the paper mill considered in this study, as well as in other existing Latin American and Caribbean mills. This study was performed in two phases, as discussed below.

Phase 1 – Field Study

This phase was completed at a paper plant in Central America in order to collect operational data that would reflect the typical variability in terms of different

machines/products. Phase 1 included field measurements such as waste/wastewater flow rate, temperature, dissolved oxygen, pH and waste/wastewater characteristics such as total and volatile solids concentrations.

Phase 2 – Laboratory Study

This phase was completed at the Georgia Institute of Technology and included the following tasks:

Sample Characterization

Eight waste/wastewater samples were obtained and chemical analysis was conducted for the following parameters: pH, soluble and total COD, total and volatile solids (TS, VS), volatile fatty acids (VFAs), nitrate, nitrite, ammonia, sulfate, and phosphate.

Batch Anaerobic Degradation Tests

These tests were performed to assess the biodegradability of the samples under ideal conditions, as well as determining the limiting rate step during the digestion of paper mill wastes. All assays were performed in triplicate and included single samples as well as combined samples. Incubation was carried out in the dark at 35˚C, an expected average temperature at the mill. Throughout the incubation period, total gas volume and composition (CH_4 and CO_2) was measured and at the end of the incubation, pH, TS, VS, COD, VFAs and ammonia were measured.

Semicontinuous Flow Anaerobic Degradation Test

In this task, the anaerobic biotreatability and methane production of two waste/wastewater combined streams were assessed. Four fed-batch, continuously stirred reactors were operated at 35^{o}C at four different retention times. Throughout this task, pH, total gas volume and composition (CH_4, CO_2), VFAs, ammonia, and phosphate were measured periodically.

CHAPTER 4

MATERIALS AND ANALYTICAL METHODS

4.1 Analyses at the Paper Mill Laboratory

4.1.1 Total Suspended Solids (TSS)

TSS were measured according to protocols used in the WWTP at the paper mill considered in this study. Briefly, 0.45 μm filters were washed with 60 ml of deionized water and dried for 1 hour at 105˚C. After temperature stabilization in desiccators, their weight (mg) was recorded using an analytical balance. Samples were vacuum filtered, and then the filters with the solids were dried for 1 hour at 105 ˚C. After temperature stabilization in desiccators, the dry filters/samples were weighted. All measurements were performed in duplicate.

TSS were calculated as follows:

$$TSS\ \left(\frac{mg}{L}\right) = \frac{(sample\ dry\ mass\ (mg) - filter\ mass\ (mg))}{volume\ of\ sample\ filtered\ (L)}$$

4.1.2 Volatile Suspended Solids (VSS)

VSS were measured according to protocols used in the WWTP at the paper mill considered in this study. The TSS dried samples were ignited for 40 minutes at 550 ˚C,

and after temperature stabilization in a desiccators, the remaining inorganic constituents were weighted.

VSS were calculated as follows:

$$VSS\ \left(\frac{mg}{L}\right) = \frac{[(weight\ after\ 105^{\circ}C - weight\ after\ 550^{\circ}C\ (mg))]}{Volume\ of\ sample\ (L)}$$

4.1.3 Total and Soluble Chemical Oxygen Demand (COD)

COD was measured using HACH's colorimetric dichromate COD Method High Range (150-1,500 mg/L) and Low Range (3-150 mg/L) method. In this method, 2 ml of sample were added to prepared COD digestion vials from HACH. The samples were incubated for 2 hours at 250 ˚C with potassium dichromate. Upon oxidation of the organic compounds, dichromate ($Cr_2O_7^{2-}$) gets reduced to green chromic ion (Cr^{3+}). When the 0-150 mg/L colorimetric method is used, the amount of Cr^{6+} remaining is determined by measuring absorbance at 600 nm. When the 0–1,500 mg/L method is used, the amount of Cr^{3+} produced is determined by measuring absorbance at 620 nm. For soluble COD, samples were filtered through 0.45 μm filters prior to the analysis.

4.1.4 Inorganic Ions

All samples were filtered prior to analysis of inorganic ions using 0.45 μm filters. Samples were diluted when needed with deionized water. All analyses were done on the same day the sample was obtained, except for sulfate during white paper production, in which case the samples were prepared and stored at 4˚C for 7-10 days prior to the analysis.

4.1.4.1 Ammonia

Ammonia was measured according to the Nessler HACH method 8038 for concentrations between 0.02 to 2.5 mg/L NH_3-N. The Nessler reagent, upon addition to a glass vial containing the diluted sample, forms a colored solution upon reaction with ammonia and other amines. A mineral stabilizer complexes hardness in the sample and a polyvinyl alcohol dispersing agent aids the formation of color. The measurements were made at 425 nm using a DR 2800 Portable Spectrophotometer (HACH; Loveland, CO).

4.1.4.2 Phosphate

Phosphate was measured according to the HACH method 8048 at a range from 0.02 to 2.5 mg/L. In this method, orthophosphate reacts with molybdate in an acid medium to produce a mixed phosphate/molybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color. Formation of color was measured at 880 nm using a DR 2800 Portable spectrophotometer (HACH; Loveland, CO).

4.1.4.3 Sulfate

Sulfate was measured according to the HACH method 8051 using Sulfate SulfaVer® 4 Reagent Powder Pillows (HACH). The principle of this method is that sulfate ions in the sample react with barium in the SulfaVer 4 reagent and form a precipitate of barium sulfate. The amount of turbidity formed is proportional to the sulfate concentration. Turbidity is measured at 450 nm using a DR 2800 Portable Spectrophotometer (HACH; Loveland, CO).

4.1.5 pH

Necessary pH measurements were obtained from on-line devices in the wastewater treatment plant, on determined waste lines.

4.2 Analyses at the Georgia Institute of Technology, Atlanta, Georgia

4.2.1 pH

All pH measurements were performed using the potentiometric method with a digital pH meter (Orion Digital pH/millivolt Meter, Model 611) and a gel-filled combination pH electrode (Fisher Scientific). For each pH measurement, a sample was transferred into a 10 ml vial and the pH was then immediately measured to minimize any artifacts due to exposure to the atmosphere. Between samples, the electrode was rinsed with deionized water and stored in an electrode storage solution (Fisher Scientific). The pH meter was calibrated weekly with pH 4.0, 7.0, and 10.0 standard buffer solutions (Fisher Scientific).

Although the sensitivity of the meter display was 0.01 units, the limit of accuracy was taken to be only 0.1 pH units (APHA 2005).

4.2.2 Total and Volatile Solids (TS and VS)

Total solids content of samples was determined according to procedures outlined in *Standard Methods* (APHA 2005). Samples were weighed in pre-ignited (550°C) and cooled ceramic crucibles using an Ohaus AP250D Analytical Balance (precise to ±0.02 mg up to 52 g, and to ±0.1 mg between 52 and 210 g). The samples were then dried at 105°C for 24 hours in a Fisher Isotemp Model 750G oven. After drying, the crucibles were transferred to a desiccator until cooled, and then the dry weight was measured. If VS were to be determined, the crucibles were transferred to a Fisher Isotemp Model 550-126 muffle furnace and ignited at 550°C for 30 minutes. After ignition, the samples were cooled in a dessicator and the remaining solids weight was measured. TS and VS were then calculated using the equations below.

$$TS\ \left(\frac{mg}{L}\right) = \frac{(Crucible\ weight\ after\ 105℃(mg) - Crucible\ tare\ weight(mg))}{Sample\ Volume\ (L)}$$

$$VS\ \left(\frac{mg}{L}\right) = \frac{(Crucible\ weight\ after\ 105℃(mg) - Crucible\ \ weight\ after\ 550℃(mg))}{Sample\ Volume\ (L)}$$

4.2.3 Total and Volatile Suspended Solids

Total suspended solids were determined according to method 2540 D as described in *Standard Methods* (APHA 2005). For this method, 2.1-mm diameter Whatman GF/C glass fiber filters (1.2 μm nominal pore size, Whatman, Springfield Mill, England) were washed with deionized water and dried at 105˚C for one hour before use. After temperature stabilization in a desiccators, the filters were then weighted in an Ohaus AP250D analytical balance. Samples of known volume were vacuum filtered and the filters containing the samples were dried at 105°C for at least 1.5 h in a Fisher Isotemp Model 750G oven. After room temperature stabilization in a dessicator, the dry weight was recorded. Total suspended solids were calculated using the following equation:

$$TSS\ \left(\frac{mg}{L}\right) = \frac{(Total\ dry\ weight(mg) - dry\ filter\ weight(mg))}{Sample\ volume\ (L)}$$

Volatile suspended solids (VSS) were determined according to procedures described in *Standard Methods* (APHA 2005). Whatman GF/C glass fiber filters (47 mm diameter and 1.2 μm nominal pore size; Whatman, Florham Park, NJ) were washed with deionized water and ignited at 550°C for 20 min in a Fisher Isotemp Model 550-126 muffle furnace before use. The filters were then cooled in a desiccators and weighed using an Ohaus AP250D analytical balance. Samples of known volume (typically 5-10 mL) were filtered and dried at 105°C for at least 1.5 h in a Fisher Isotemp Model 750G oven. After cooling down in a desiccators, the dry weight was recorded and the filters containing dry samples were transferred to a Fisher Isotemp Model 550-126 muffle furnace and ignited at 550°C for 30 min. After ignition, the samples were again left in a desiccators to cool to room

temperature. The residual solids weight was measured, and then the VSS concentration was calculated as follows:

$$VSS\ \left(\frac{mg}{L}\right) = \frac{(Filter\ weight\ after\ 105℃\ (mg) - Filter\ weight\ after\ 550℃(mg))}{Sample\ volume\ (L)}$$

4.2.4 Gas Production and composition

4.2.4.1 Gas production

Total gas production was measured by inserting a needle connected to a water-containing graduated burette into the headspace, and measuring the displacement of the water equilibrated to atmospheric pressure. All gas volume data reported are at 35˚C and 1 atm.

4.2.4.1 Gas Composition

The gas composition was determined by a gas chromatography (GC) unit (Agilent Technologies, Model 6890N; Agilent Technologies, Inc., Palo Alto, CA) equipped with two columns and two thermal conductivity detectors. Methane (CH_4) was separated from the mixture with a 15 m HP-Molesieve fused silica, 0.53 mm i.d. column (Agilent Technologies, Inc.). Carbon dioxide (CO_2) was separated from the mixture with a 25 m Chrompac PoraPLOT Q fused silica, 0.53 mm i.d. column (Varian, Inc., Palo Alto, CA). Helium was used as the carrier gas at a constant flow rate of 6 mL/min. The 10:1 split injector was maintained at 150^{o}C, the oven was set at 40^{o}C and the detector temperature was set at 150^{o}C. All gas analyses were performed by injecting a 100 µL gas sample. The minimum detection limit for CH_4 and CO_2, was 500 and 800 ppmv, respectively.

4.2.5 Volatile Fatty Acids (VFAs)

VFAs (C_2 to C_7, i.e., acetic, propionic, iso-butyric, n-butyric, iso-valeric, n-valeric, iso-caproic, n-caproic and heptanoic acids) were measured after acidification of filtered samples with a 2.5% v/v H_3PO_4 solution containing 1.5 g/L acetoin as the internal standard (sample:acid solution, 2:1 volume ratio) using an Agilent 6890 Series GC unit equipped with a flame ionization detector and a 35-m Stabilwax-DA, 0.53-mm I.D. column (Restek, Bellefonte, PA). Samples used for the measurement of VFAs were prepared by centrifugation at 10,000 rpm for 30 minutes and filtration through 0.22 μm PVDF membrane filters before acidification. The minimum detection limit for each acid mentioned above was 0.25, 0.10, 0.03, 0.02, 0.10, 0.08, 0.02, 0.02, and 0.05 mM, respectively.

4.2.6 Organic Acids

Non-flame ionizable organic acids (formic, oxalic, citric, malic, pyruvic, lactic, succinic and fumaric acids), alcohols (methanol, ethanol, and butanol), and carbohydrates (glucose) were measured with a HP 1100 Series HPLC (Hewlett Packard, Palo Alto, CA) unit equipped with an Aminex HPX-87H ion exclusion column (300 × 7.8 mm)(Bio-Rad, Richmond, CA) and an Agilent 1100 Series UV/visible diode array and refractive index detectors (Agilent Technologies, New Castle, DE). A 0.01 N H_2SO_4 solution was used as the mobile phase with a flow rate of 0.6 mL/min and the column was maintained at 65ºC.

The samples were centrifuged and the supernatant was acidified with 0.2 N H_2SO_4 in a 1:1 ratio, and filtered through 0.2 μm membrane filters before the analyses. Organic acids were detected by the UV detector at 210 nm wavelength.

4.2.6 Ions

Measurements for nitrate (NO_3^-) nitrite(NO_2^-) phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}) were conducted using a Dionex DX-100 Ion chromatography unit (Dionex Corporation, Sunnyvale, CA) equipped with a suppressed conductivity detector, a Dionex IonPac AG14A (4x50mm) precolumn, and a Dionex IonPac AS14A (4x250 mm) analytical column. The unit was operated in autosupression mode with 1 mM $NaHCO_3$/8 mM Na_2CO_3 eluent and a flow rate of 1 mL/min. All samples were filtered through 0.2 μm membrane filters prior to injection. The minimum detection limit for each anion listed above was 0.02, 0.04, 0.02 and 0.05 mM, respectively.

4.2.7 Ammonia

The ammonia distillation method per *Standard Methods* (APHA 2005) was used to determine the liquid phase ammonia concentration in all wastewater and culture samples. All samples were centrifuged at 12,000 rpm for 15 minutes and filtered through a 0.2 μm membrane filter (Fisher Scientific, Pittsburgh, PA). Then, the samples were added to an ammonia distillation apparatus (Labconco Corp., Kansas City, MO). The pH of all samples was kept at 9.5 by addition of NaOH to a final concentration of 1.8 N and borate buffer was added to increase hydrolysis of organic nitrogen compounds (APHA 2005).

Ammonia vapors from the boiling samples were condensed and captured through the immersed outlet of the distillation apparatus in indicating boric acid solution. Ammonia captured in the solution was quantified by titration with 0.2 N H_2SO_4.

4.2.8 Methanogenic culture and media

4.2.8.1 Methanogenic culture

The original inoculum of the culture used in the present study was obtained from a mesophilic (35˚C), municipal anaerobic digester. The culture was maintained at 35˚C and was fed twice a week with a concentrated dextrin/peptone solution (8 g/L dextrin, 4 g/L peptone) and nutrient media, with a hydraulic retention time of 35 days. The feed corresponds to an average organic loading rate of 0.34 g COD/L-day. The steady-state gas-phase methane and carbon dioxide content of this culture was 60.77 ±0.5% and 39.27±0.4% (mean ± standard deviation), respectively. The steady-state total (TS) and volatile solids (VS) concentration of this culture was 6.97±0.3 and 2.27±0.1 g/L (mean ± standard deviation), respectively (Tezel et al. 2006). The culture was kept continuously mixed with a magnetic stirrer, and was maintained under the above-stated conditions for over five years before the initiation of this study.

4.2.8.2 Methanogenic culture media

The mixed methanogenic culture used in this study was sustained in a medium which supplied necessary nutrients, trace metals, and vitamins. The composition of the culture media is shown in Table 4.1. Resazurin was used as a redox indicator (ORP < -110 mV). Culture media were prepared by adding the first six ingredients in Table 4.1 to 8 L DI water in 9-L Pyrex serum bottles. The bottles were then autoclaved at 250^{o}F (121^{o}C) and

21 psi (1.43 atm) for 45 minutes. After autoclaving, the bottles' contents were purged with helium for 1.5 hours in order to strip oxygen from the media. After purging, and while the media were still warm, the rest of the ingredients listed in Table 4.1 were added.

Table 4.1. Composition of media for the mixed anaerobic culture used in this study

Compound/Solution	**Concentration**
K_2HPO_4	0.9 g/L
KH_2PO_4	0.5 g/L
NH_4Cl	0.5 g/L
$MgCl_2 \cdot 6H_2O$	0.2 g/L
Trace metal stock solution	1 mL/L
1 g/L resazurin stock	2 mL/L
Vitamin stock solution	1 mL/L
$CaCl_2 \cdot 2H_2O$	0.1 g/L
$FeCl_2 \cdot 4H_2O$	0.1 g/L
$NaHCO_3$	3.5 g/L
$Na_2S \cdot 9H_2O$	0.5 g/L

Trace metal stock solution	**Concentration**
$ZnCl_2$	0.5 g/L
$MnCl_2 \cdot 4H_2O$	0.3 g/L
H_3BO_3	3.0 g/L
$CoCl_2 \cdot 6H_2O$	2.0 g/L
$CuCl_2 \cdot 2H_2O$	0.1 g/L
$NiSO_4 \cdot 6H_2O$	0.2 g/L
$Na_2MoO_4 \cdot 2H_2O$	0.3 g/L

Vitamin stock solution	**Concentration**
Biotin	0.2 g/L
Folic Acid	0.2 g/L
Pyridoxine hydrochloride	1.0 g/L
Riboflavin	0.5 g/L
Thiamine	0.5 g/L
Nicotinic Acid	0.5 g/L
Pantothenic Acid	0.5 g/L
Vitamin B12	0.01 g/L
p-Aminobenzoic Acid	0.5 g/L
Thioctic Acid	0.5 g/L

CHAPTER 5

PLANT VARIABILITY AND SAMPLE CHARACTERIZATION

5.1 Introduction

The current solid waste management approach used in the study paper mill consists of mechanical dewatering steps and transport and disposal of the resulting solid waste in landfills. The proposed alternative is to treat these solid wastes anaerobically. As a paper manufacturing plant, most of the solid wastes are ligno-cellulosic in nature, which are hydrolysable and biodegradable. However, all of the fiber used in this plant is secondary fiber (from recycled paper), and therefore the composition is not known. Moreover, different chemicals, such as those periodically added, result in a complex mixture with unknown properties. For this phase of the study, the objectives were to characterize, through key parameters, the wastes generated in the manufacturing and wastewater treatment processes, as well as to examine the variability of the plant operation in order to select the appropriate samples and sampling frequency for subsequent experimentation for anaerobic digestion, and to determine whether the conditions are appropriate for implementation of anaerobic process(es) in the overall waste management.

5.2 Sample characterization

5.2.1 Plant variability

As explained in Chapter 4, at the study paper mill, two major types of tissue paper are produced: white and "natural". These types are produced using different types of recycled paper of unknown composition, potentially resulting in the generation of solid wastes with different properties. The type of tissue produced in the study paper mill is directly based on consumer behavior and demand, and changes accordingly. Therefore, in order to determine the appropriate sampling frequency for laboratory experiments, it was important to study the variability of the process and the wastes generated.

In order to determine the effect of the variability of paper production on the characteristics of specific waste streams, the system was analyzed in a period that comprised both production schemes. To achieve this, eight samples were selected for characterization from different points of the processes to study their anaerobic biodegradability, and periodical analyses of a number of operational parameters were conducted for four weeks, to capture the two full cycles of production for both white and "natural" paper. The sampling points are shown in Figure 5.1 and described in Table 5.1.

5.2.2 Sample Characterization at the Georgia Institute of Technology

After the periodical monitoring of several parameters of the system, samples from eight points from the study plant (Table 5.2) were shipped to Georgia Tech to be used in laboratory experiments. For that purpose, each stream was characterized upon arrival.

Table 5.1. Monitoring points at the study paper mill

	Sample	Description	Unit Process	Description
Manufacturing	1	Flotation Cell Skimmings	Deinking	Removal of ink from recycled paper using a flotation system
	3	Mill DAF Skimmings	Paper Manufacturing	Dissolved air flotation for solids separation during manufacturing process (recirculation of water)
Wastewater Treatment	5	WWTP DAF Influent	Primary Treatment	Dissolved air flotation for solids removal. Underflow is activated sludge influent.
	7	WWTP DAF Underflow		
	9	Aeration Tank	Secondary Treatment	Activated sludge process
	8	Waste Activated Sludge (WAS)		

Note: Samples 2, 4, and 6 were not included in the original plant sampling plan

Table 5.2. Sample origin at the study paper mill

	Sample	Description	Unit Process	Description
Manufacturing	1	Flotation Cell Skimmings	Deinking	Removal of ink from recycled paper using a flotation system
	2	Flotation Cell Underflow		
	3	Mill DAF Skimmings	Manufacturing	Dissolved air flotation for solid separation during manufacturing process (recirculation of water)
	4	Mill DAF Underflow		
Wastewater Treatment	5	WWTP DAF Influent	Primary Treatment	Dissolved air flotation for solid removal. Underflow is activated sludge influent.
	6	WWTP DAF Skimmings		
	7	WWTP DAF Underflow		
	8	Waste Activated Sludge (WAS)	Secondary Treatment	Activated sludge process

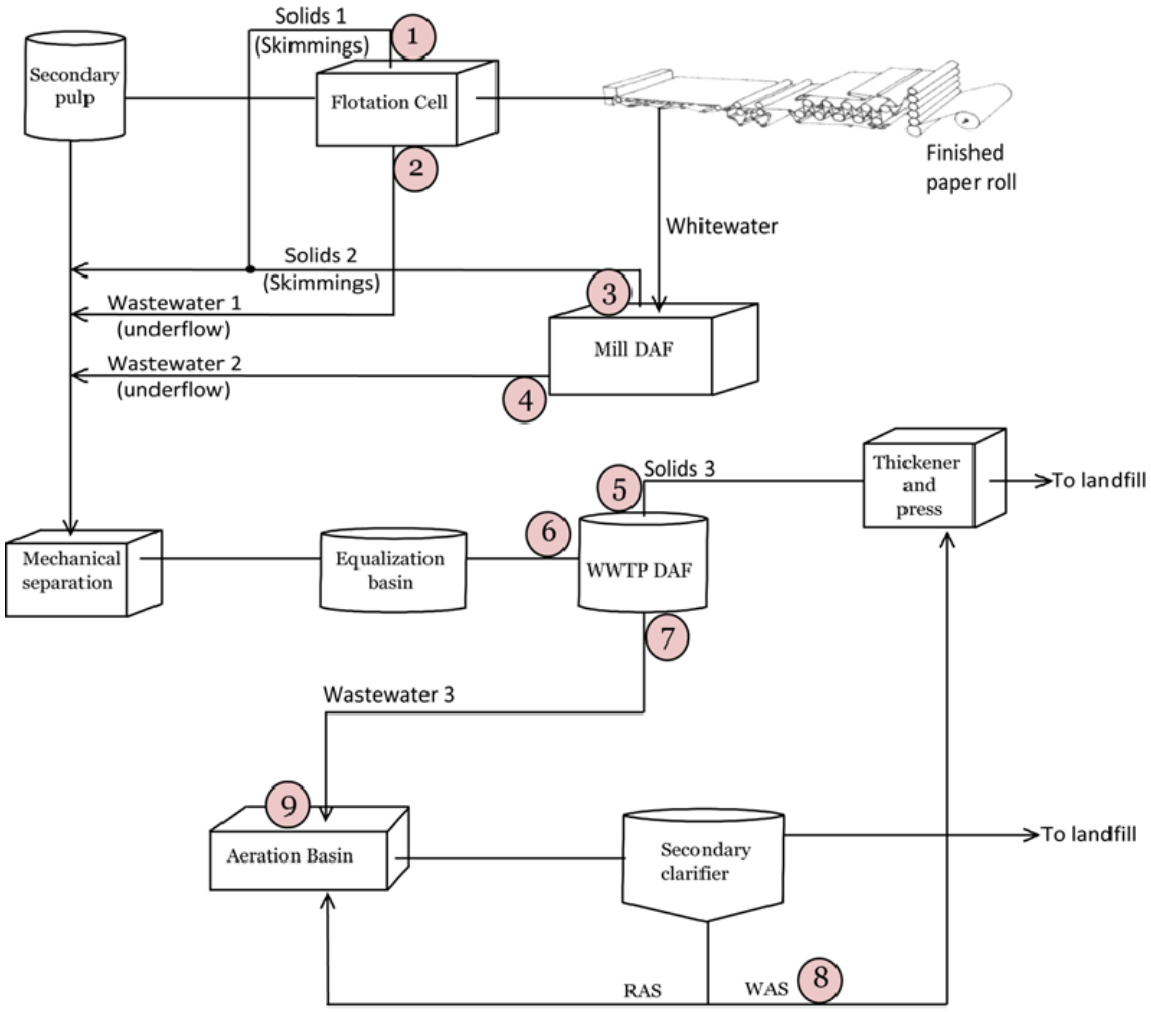

Figure 5.1. Simplified scheme of the manufacturing and wastewater treatment plant at the study paper mill (Summer 2008). Sample numbers 1-9 correspond to those referenced in Tables 5.1 and 5.2.

5.3 Materials and Methods

5.3.1 Characterization at the Paper Mill

The characterization of the waste streams was carried out in the laboratory located at the wastewater treatment plant at the study paper mill. All of the samples were obtained on the same day of analysis. Tissue production is continuous every day, 24 hours a day, so samples obtained for analysis can be assumed to be representative of the process. Each production period lasted two weeks, and therefore sampling frequency was scheduled to be of three times per week, for four weeks. Samples were obtained from the aeration basin, return activated sludge lines, the mill DAF skimmings, and the wastewater treatment plant (WWTP). The samples consisted of the DAF skimmings from the process mills, DAF influent and underflow from the WWTP, mixed liquor activated sludge, and return activated sludge. A simplified scheme of the waste streams is shown in Figure 5.1, and in Table 5.1. Measurements of suspended solids, volatile suspended solids, ammonia, sulfate, phosphate, and COD were carried out for all samples.

5.3.2 Characterization of Select Samples for Laboratory Studies

All samples were collected by plant personnel at the study paper mill and shipped refrigerated at 4^{o}C to the Georgia Tech Laboratory, in Atlanta GA. Aliquots were analyzed upon arrival for pH, COD, TS, VS, ammonia, nitrate, nitrite, phosphate, sulfate and volatile fatty acids according to methods described in Chapter 4 . The remaining sample volume was stored in firmly closed buckets and kept at 4^{o}C for subsequent utilization in batch and semicontinuous flow reactor experiments.

5.4 Results and Discussion

5.4.1 Characterization at the Paper Mill

All the samples obtained from the different points of operation were analyzed on the same day either for TSS, COD or nutrients, or filtered and stored at 4^{o}C for analysis on the following day. Analyses were carried out for two cycles of operation, one for white and the other for natural paper. The samples were analyzed for TSS, pH, COD, NH_4, PO_4 and SO_4 and results are listed in Tables 5.3 and 5.4. The results show that none of these parameters vary substantially among the two processes. A graphical comparison is shown in Figure 5.2 for parameters related to the manufacturing process.

The wastewater treatment plant receives very high loadings of solids and COD but after removal of solids in the WWTP DAF, the activated sludge aeration tank receives a relatively low concentration of solids and COD (<500 mg/L and <900 mg/L, respectively). Most of the solids that can be utilized for methane production are disposed of in landfills, untreated, after dewatering. Most of the COD is, therefore, not revalorized.

It is notable that the value of solids for the aeration basin was unusually high compared to typical values of 3,000-6,000 mg/L found in typical tissue mill aerobic activated sludge units (Thompson et al. 2001), and so was the WAS, which is due to the design of this particular wastewater treatment system in the study paper mill.

Recycled paper has a very high carbon to nitrogen and phosphorus ratio, as the main waste components consist of cellulose, hemicellulose, and inorganic constituents. These nutrients increase in samples taken from the wastewater treatment plant due to the

addition of urea and phosphoric acid to the aeration basin, supplemented to maintain the proper conditions for the biological oxidation of the influent organics. In anaerobic processes it is expected that nutrient addition will be less demanding compared to aerobic processes as discussed in Chapter 3.

Table 5.3. Waste streams variation at the study paper mill (July 2008)–TSS, VSS, pH, and COD (mean ± standard deviation; *n = 6*)

Tissue type	Waste type	TSS (g/L)	VSS (g/L)	pH	COD (mg/L)
White	Flotation cell skimmings	53.2±5.7	6.2	ND	29850±4409
	Mill DAF skimmings	8.8±3.3	3.3±1.8	ND	11275±4375
	DAF underflow	0.5±0.4	0.3±0.4	8.3±1.0	917±211
	Aeration Tank	15.5±2.9	9.4±2.5	7.7±0.8	10723±936
	Final Effluent	0.2±0.1	ND	6.9±0.2	180±85
	RAS/WAS	18.2±2.2	13.3±0.8	ND	12321±2165
Natural	Flotation cell skimmings	48.6±9.5	29.4	ND	30675±8488
	Mill DAF skimmings	6.8±2.8	4.4±1.5	ND	7225±4186
	DAF underflow	0.3±0.2	0.1±0.1	7.2±0.2	876±227
	Aeration Tank	10.1±0.3	6.2±0.2	7.8±0.2	6640±317
	Final Effluent	ND[a]	ND	6.9±0.1	56±82
	RAS/WAS	14.0±0.8	7.9±1.8	ND	9124±3399

[a] ND, not determined

Table 5.4. Waste streams variation at the study paper mill (July 2008)–Nutrients (mean ± standard deviation; *n* = 6)

Tissue type	Waste type	NH_4^+-N (mg/L)	PO_4^{3-}-P (mg/L)	SO_4^{2-}-S (mg/L)
White	Flotation cell skimmings	2.4±1.2	0.1±0.0	ND[a]
	Mill DAF skimmings	1.8±1.1	0.2±0.2	68.0±73.5
	DAF underflow	3.6±0.7	1.1±1.9	54.8±5.7
	Aeration Tank	1.5±0.8	5.8±1.0	64.0±
	Final Effluent	2.9±1.1	2.7±1.9	ND[a]
	RAS/WAS	2.5±0.7	6.8±1.5	57.4±7.4
Natural	Flotation cell skimmings	2.2±0.4	0.1±0.1	117.0±18.6
	Mill DAF skimmings	1.8±0.6	0.1±0.0	111.4±30.4
	DAF underflow	3.0±1.7	1.2±2.6	96.6±16.2
	Aeration Tank	0.3±0.2	4.4±2.6	110.0±15.1
	Final Effluent	0.8±1.2	5.9±2.2	76.6±20.3
	RAS/WAS	0.8±0.4	6.0±2.0	103.0±16.5

[a]ND, not determined

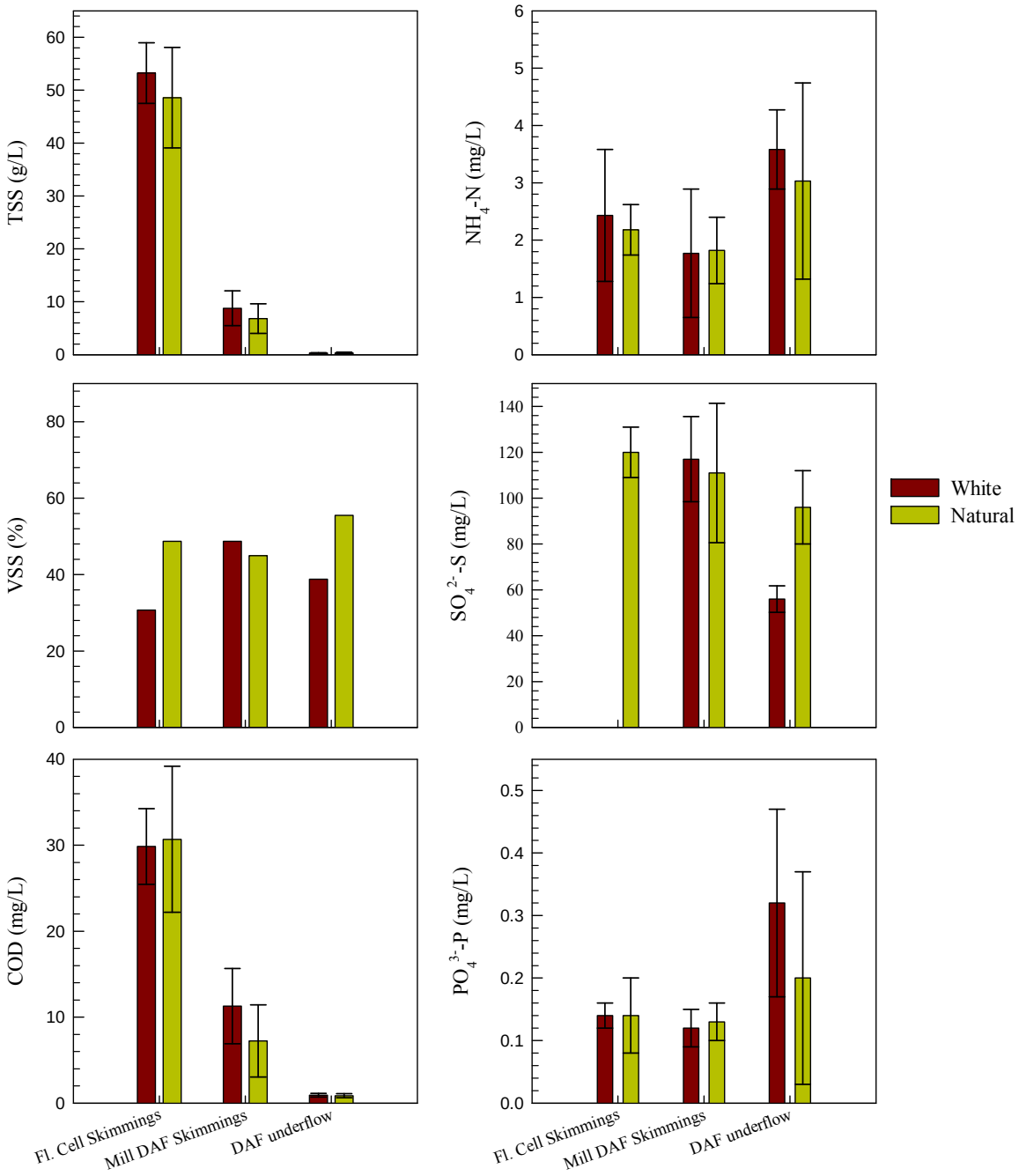

Figure 5.2. Waste stream variation at the study paper mill. Samples were taken periodically for four weeks and analyzed for solids, COD and nutrients, and compared between the two production schemes (i.e., white vs. natural paper). Only waste streams from the manufacturing plant are shown in this figure (Error bars are standard deviations; $n = 6$).

5.4.2 Characterization of Select Samples for Laboratory Studies

Eight samples were characterized for pH, total and soluble COD, total and volatile solids, volatile fatty acids and inorganic species and the results are summarized in Tables 5.5 to 5.7. All of the samples had similar pH values of 6-6.5, which could be detrimental to methanogens.

The chemical oxygen demand is very high in all skimming samples, which, if degradable, would make these samples very suitable for anaerobic digestion. All samples have low levels of a mixture of volatile fatty acids, probably due to a small period of anoxic conditions prior to arriving to the wastewater treatment plant. Nitrate and nitrite were not detected, and sulfate was present in all samples, at different concentrations. Sulfate reduction might compete with methanogenesis.

Finally, neither ammonia nor phosphorus was detected in any sample, which is consistent with the origin of the waste samples, i.e., recycled paper. Addition of nitrogen and phosphorus will need to be implemented for the anaerobic treatment.

Table 5.5. Sample characterization – pH and COD (mean ± standard deviation; *n* = 3).

Sample	pH	Total COD (mg/L)	Soluble COD (mg/L)	Soluble %
1	6.16	30298±925	865±73	2.9
2	6.12	33509±839	983±42	2.9
3	6.55	8577±2036	493±10	5.8
4	6.31	740±61	407±36	55.0
5	6.1	36212±1303	733±124	2.0
6	6.06	29426±381	1375±112	4.7
7	6.14	555±16	571±45	103.0
8	5.97	12085±520	409±48	3.4

Table 5.6. Sample characterization – Solids and VFAs (mean ± standard deviation; *n* = 3).

Sample	VFAs (mg COD/L)	Solids		
		Total (mg/L)	Volatile (mg/L)	Volatile (%)
1	317.8	9004±925	865±73	9.6
2	287.0	33509±839	983±42	2.9
3	126.8	8577±2036	493±10	5.8
4	83.0	740±61	407±36	55.0
5	212.8	9004±301	4345±56	48.3
6	389.0	35560±662	17784±398	50.0
7	127.0	103±9	107±8	103.9
8	212.3	7629±73	3552±149	46.6

Table 5.7. Sample characterization – Anions.

Sample	Anions (mg/L)		
	SO_4^{2-}-S (mg/L)	NO_3^-/NO_2^--N (mg/L)	PO_4^{3-}-P (mg/L)
1	29.6	ND[a]	ND[a]
2	29.0		
3	6.6		
4	3.0		
5	36.6		
6	24.9		
7	49.9		
8	48.6		

[a] ND, not detected

CHAPTER 6

BATCH ANAEROBIC BIODEGRADABILITY ASSAYS

6.1 Introduction

The anaerobic digestion of wastes has the potential to reduce solids as well as to generate a usable form of fuel (methane gas). Different sources of wastes from a variety of industrial processes can be digested in this way, such as domestic wastewater, sludge and agricultural wastes (Noyola et al. 2006). However, even though cellulosic material could be reduced prior to disposal and serve potentially as a methane source, very limited research has been conducted on the anaerobic digestion of paper mill solid wastes. This is primarily because in recent years many plants have been converted to a pulp-only or paper-only operation, as opposed to pulp and paper, and the waste streams in these plant configurations have not been studied in detail. Furthermore, since paper plants rely on post-consumer paper, the characteristics of the wastes generated vary from plant to plant, and it is therefore important to conduct plant-specific analyses and bioassays.

The objective of this phase of the study was to determine the anaerobic biodegradability of selected waste streams generated at the study paper mill, as well as to assess any potential toxicity in single streams under ideal, laboratory conditions.

6.2 Materials and Methods

6.2.1 Samples

The samples used for all batch assays were obtained from the study paper mill, as explained in Chapter 4 and were kept at 4˚C upon arrival until used. Each sample was tested alone (sample 1 through 8), and in combinations (Feed 1 and 2) to assess their ultimate biodegradability under methanogenic conditions.

6.2.2 Methanogenic Culture

The mixed, methanogenic culture used in the batch assays was obtained from a culture maintained in the laboratory. The original inoculum was obtained from a mesophilic (35˚C), municipal anaerobic digester, as explained in Chapter 3. The culture was maintained at 35˚C and was fed twice a week with a concentrated dextrin/peptone solution (8 g/L dextrin, 4 g/L peptone) and nutrient media, with a hydraulic retention time of 35 days. The volatile solids (VS) concentration of this culture was 6.9±0.3 and 2.2±0.1 g/L (mean±standard deviation), respectively (Tezel *et al.* 2006). The culture is kept continuously mixed with a magnetic stirrer, and was maintained under the above-stated conditions for over five years before the initiation of this study.

6.2.3 Ultimate Biodegradability Assays

6.2.3.1 General Experimental Setup

For all batch assays, 160 ml glass serum bottles were used, with a liquid volume of 120 ml. All serum bottles were amended with the samples, and DI water, and then flushed with helium for 10 minutes, prior to the addition of the methanogenic culture and media with plastic syringes in order to ensure anaerobic conditions. The general set up of the

assays is shown in Table 6.1. All incubations were carried out at 35˚C and the bottles were shaken manually on a daily basis. Measurements of gas production and composition were carried out periodically during the incubation period. The volume of gas produced was measured by displacement of water in a graduated burette after equilibrating to atmospheric pressure, and gas composition in terms of methane and carbon dioxide was measured by gas chromatography as described in Chapter 3. At the end of the incubation period, total and volatile solids, COD, pH and VFAs were measured to determine the biodegradability of each sample.

COD destruction was calculated as follows:

$$COD\ destruction\ (\%) = \left[\frac{COD\ added - COD\ remaining}{CODadded}\right] x100 \qquad (6.1)$$

The same equation was used for solids destruction.

In order to ensure that COD destruction and methane production matched, a COD balance was performed at the end of the incubation period as follows:

$$COD\ balance\ \% = \frac{[CODin - (CODfinal + CODmethane)]\ (mg)}{CODin\ (mg)} x\ 100 \qquad (6.2)$$

Methane COD was calculated according to the theoretical value of 0.35 L/g COD destroyed at STP (0^oC and 1 atm) and corrected for temperature (308 K). Then, since 394.9 ml methane are produced per g COD destroyed at 35^oC,

$$methane\ COD\ (mg) = \frac{ml\ methane\ produced}{394.9\ ml\ methane.gCOD^{-1}}\ x\ \frac{1000\ mg}{g}\ . \qquad (6.3)$$

Also, to obtain an indirect measure of the biodegradability of the samples, the methane production per gram of COD consumed (i.e., the specific methane production, SMP; ml CH_4 at 35°C/g COD destroyed) was calculated as:

$$SMP\ at\ 35^{\circ}C\ \left(\frac{mL}{g}\right) = \frac{ml\ methane\ produced}{gCOD(in-final)} \quad (6.4)$$

and the relative SMP as:

$$Relative\ SMPat\ 35℃ = \frac{SMP\ (\frac{mL}{g})}{394.9\ mL\ methane/gCOD} \quad (6.5)$$

Table 6.1. Experimental Setup for All Batch Assays.

Parameter	Value
Total Volume, mL	160
Volume of Head Space, mL	40
Working Liquid Volume, mL	120
Methanogenic Culture, mL	60
Methanogenic Culture COD loading, g/L	1.7
Culture Media, mL	18

6.2.3.2 Biodegradability Assay of Single Samples (Assay I)

Solids and whitewaters are discharged at several points during the manufacturing and wastewater treatment processes. In order to select which streams are treatable, it is necessary to determine the amount of biodegradable material and the potential of methane generation, as well as their potential toxicity for methanogens. Therefore, with the objective of determining the ultimate biodegradability of single streams, batch assays were conducted for the eight characterized individual samples obtained from the study paper mill (see Chapter 5 for sample identification).

For this assay, a fixed COD level of 3 g/L of sample was added in each bottle, except in the case of samples 4 and 7, which were very dilute. For these two samples, the bottles were filled with each sample to the maximum volumetric capacity (the volume left after addition of culture and media) rendering a COD value of 259 and 194 mg/L, respectively. One bottle series received only the methanogenic culture and water (seed blank). A reference series was also included with dextrin and peptone with a COD value of 1.2 g/L. All culture series were prepared in triplicate. A summary of the batch assay I setup is given in Table 6.2.

Table 6.2. Details of Batch Assay I Setup[a, b].

Culture Series	Sample	Sample mL	DI Water mL	Working Volume mL	COD mg	COD mg/L
Seed Blank		0.0	42.0	120	360	
Dextrin/Peptone		0.0	0.0	120	144	1200
FC skimmings	1	11.9	30.1	120	360	3080
FC underflow	2	10.7	31.3	120	360	3071
MD skimmings	3	42.0	0.0	120	360	3408
MD underflow	4	42.0	0.0	120	31	258
WWTP influent	5	24.9	17.1	120	360	1207
WWTP skimmings	6	12.1	29.9	120	360	2991
WWTP underflow	7	42.0	0.0	120	23	194
WAS	8	29.8	12.2	120	360	3011

[a] Abbreviations: FC, flotation cell; MD, Mill DAF; WWTP, wastewater treatment plant; WAS, waste activated sludge

[b] Culture and media volume, 60 and 18 mL, respectively, in all culture series

6.2.3.3 Ultimate Biodegradability of Combined Samples (Assay II)

In this batch assay, two combinations of wastes were tested: a mixture of the flotation cell skimmings and the mill DAF skimmings (Feed 1) and a combination of the wastewater treatment plant DAF skimmings and WAS (Feed 2). For this second combination, three different ratios of skimmings to WAS were tested, assuming that different volumes of skimmings were taken out from the WWTP DAF: 5, 10, and 15% of the total flotation cell flow rate, and a constant volume of WAS, according to the flow rate employed in the plant. Therefore, the following WWTP DAF skimmings:WAS ratios were tested: 0.6:1, 3:1 and 6:1. For the flotation cell skimmings and mill DAF skimmings, a ratio of 1:2.6 was tested. All waste combinations were assessed in triplicate for 90 days while measurements of gas production and composition were made. In addition, the initial and

final COD levels, total and volatile solids, VFAs and pH were measured. A summary of the batch assay setup is given in Table 6.3

Table 6.3. Details of Batch Assay II Setup[a,b].

Component	WWTP DAF:WAS			FC:Mill DAF (Feed 1)
	0.6:1	3:1 (Feed 2)	6:1	1:2.6
Sample 6 - WWTP DAF skimmings (mL)	6	9	12	--
Sample 8 – WAS (mL)	10	3	2	--
Sample 1 – FC (mL)	--	--	--	1.7
Sample 3 - Mill DAF skimmings (mL)	--	--	--	4.33
DI Water (mL)	26	30	28	36
COD/L (mg/L)	2,478	2,509	3,144	770

[a] Abbreviations: FC, flotation cell; WWTP, wastewater treatment plant; DAF, dissolved air flotation; WAS, waste activated sludge

[b] Culture and media volume, 60 and 18 mL, respectively, in all culture series

6.3 Results and Discussion

6.3.1 Ultimate Biodegradability of Single Waste Streams (Assay I)

Eight samples from the study paper mill were assessed for their biodegradability in a batch assay and compared to a reference sample of dextrin and peptone. The incubation period was 90 days. The initial and final composition was compared, as well as the evolution of total gas, methane and carbon dioxide, in order to determine the extent of anaerobic degradation of each waste sample under ideal, batch conditions. The results obtained for each of these parameters are shown in Tables 6.4 and 6.5, and discussed below.

Table 6.4. Results for ultimate biodegradability of samples 1 to 4 (Assay I; seed blank corrected).

Parameter	Sample			
	1	2	3	4
Initial pH	7.14	7.1	7.1	7.1
Final pH	6.74	6.86	7.08	7.25
Initial total COD, mg/L	3080	3071	3408	259
Final total COD, mg/L	1708	1381	2676	ND[a]
Total COD destruction,%	44.6	55	21.5	ND[a]
Initial TS, mg/L	1761	1738	1606	50
Final TS, mg/L	439	431	940	285
TS destruction, %	75.1	75.2	41.5	ND[a]
Initial VS, mg/L	1553	1479	913	40
Final VS mg/L	226	186	377	191
VS destruction, %	85.4	87.4	58.7	ND[a]
Total gas produced/g COD added, mL at 35˚C	296.1	276.4	145.3	373.0
CH_4 produced/g COD added, mL at 35˚C	166.0	158.0	78.0	223.7
CH_4 , %	56	57	57	57
COD Balance	0.09	12.4	0.95	ND[a]
Relative specific methane production	0.99	0.77	0.96	0.31

[a] ND, not determined

Table 6.5. Results for ultimate biodegradability of samples 5 to 8 and reference (Assay I; seed blank corrected).

Parameter	Sample				
	5	6	7	8	Reference
Initial pH	7.11	7.16	7.16	7.17	6.94
Final pH	7.18	6.90	7.30	7.17	6.96
Initial total COD, mg/L	1207	2991	194	3011	1200
Final total COD, mg/L	584	1094	ND[a]	1654	56
Total COD destruction,%	51.6	63.4	ND[a]	45.0	95.3
Initial TS, mg/L	750	7230	36	1907	1235
Final TS, mg/L	521	5301	659	1622	68
TS destruction, %	30.6	26.7	ND[a]	15.0	94.5
Initial VS, mg/L	362	3616	114	888	1200
Final VS mg/L	173	1367	140	665	245
VS destruction, %	52.2	62.2	ND[a]	25.1	79.6
Total gas produced/g COD added, mL at 35˚C	404.8	321.5	394.9	133.0	540.0
CH_4 produced/g COD added, mL at 35˚C	133.0	192.2	234.9	84.0	323.5
CH_4, %	61	56	56	63	59
COD Balance	8.08	11.07	ND[a]	20.75	-2.45
Relative specific methane production	0.84	0.82	0.34	0.54	1.03

[a] ND, not determined

6.3.1.1. Chemical Oxygen Demand Destruction

The chemical oxygen demand was reduced in all samples as shown in Tables 6.4 and 6.5. The COD destruction ranged from 21 to 63%, the highest value corresponding to the WWTP DAF skimmings, and the lowest to the manufacturing mill DAF skimmings. The flotation cell skimmings and underflow also had a high portion of biodegradable COD, between 40 and 50%. This is expected, since deinking sludge usually has a high content of organic material, and these samples had a VS content of 88 and 86% of TS, respectively. The mill DAF skimmings, on the other hand had a 57% VS of the TS, which is consistent with the lower COD reduction obtained in the batch assay.

The DAF influent and skimmings had similar COD biodegradability (51 and 64%, respectively), with relative specific methane production of 0.82 and 0.84, which is expected since these samples have an almost identical composition. The DAF skimmings do not contain the soluble portion of the influent (i.e., the underflow), plus they contain flotation polymers which may explain the slight increase in degradability.

For the Mill and WWTP DAF underflows, since the amount of COD added was very small compared to the culture seed (about an order of magnitude lower), the COD results obtained at the end of the incubation period are difficult to interpret. In these series, the COD consumed comes from the samples as well as from the methanogenic culture seed, but considering that the volatile solids content of these samples was around 90%, it is probable that all of the COD added was degraded under the test methanogenic conditions. In fact, in the aerobic wastewater treatment, there is typically 95% of BOD consumption achieved for the WWTP DAF underflow. The trend of methane production was similar to

the rest of the series and no delay was observed for methane production, indicating that there should not be any major interfering soluble compounds in these samples.

The final values of soluble COD were below 300 mg/L in all cases and the seed blank had a value of 200 mg/L. From these values it can be seen that the process proceeded all the way either to methanogenesis or anaerobic respiration. Otherwise, a large value of soluble COD would have indicated that hydrolysis, but not subsequent steps, were occurring.

6.3.1.2 Solids Destruction

Solids generated in the deinking and manufacturing skimmings were substantially reduced, achieving values of 75 and 41.5 % destruction, respectively. These results are consistent with the COD reduction differences observed between these two samples.

In terms of total and volatile solids, the WAS sample had the least degradable solids, 15 and 25%, respectively. Solids destruction values for all single samples are given in Table 6.4 and 6.5. As was the case with COD reduction, the WWTP DAF influent and skimmings had similar solids destruction, consistent with the fact that these samples have an almost identical composition. For both of the underflows, solids destruction could not be determined accurately, again, due to the low amount of solids added compared to the culture seed.

6.3.1.3 Methane Production

Methane was produced in all samples, with a gas content of around 60% methane and 40% carbon dioxide. The gas methane content was in the range of 58-66% (Table 6.4 and 6.5). Figure 6.1 shows the cumulative total gas production per gram of COD added, as

well as methane and carbon dioxide throughout the incubation period, for all samples. As shown by these data, for all samples most of the gas production occurred by day 40, with very minimal gas production after this time. Taking into consideration the amount of COD destroyed and comparing that number with the relative specific methane production, COD released as methane per gram of COD destroyed, it can be determined how biodegradable the samples are, and how much of that reduction was due to methanogenesis. Values for relative specific methane production are included in Tables 6.4 and 6.5. For most cases, the relative specific methane production was above 0.8, indicating that methanogenesis was the predominant form of anaerobic metabolism, regardless of the biodegradability extent of the samples. The only sample that had a low value of relative specific methane production was the WAS. One of the reasons is the competition with sulfate reducers, as the concentration of sulfate in this sample (as well as in the WWTP DAF underflow) was about 50 mg sulfate-S/L. The rates of methane production in these samples also suggest that more than one anaerobic metabolic process is taken place, as explained below. If one considers that 2 mg of COD are consumed per mg of SO_4^2-S reduced to S(-II), this would result in about 100 mg COD/L being consumed if 50 mg/L of SO_4^{2-} are present. This contribution, although significant, is still not enough to explain the total of the COD consumed but not evolved as methane.

In single samples corresponding to the DAFs underflows (samples 4 and 7), the determination of COD and solids destruction was difficult given the diluted nature of these samples. However, comparing the gas production curves for these samples to that of the seed blank shows that no major inhibition of methanogenesis took place. Furthermore, sample 5, (WWTP DAF) influent had a comparable COD and solids

destruction to sample 6 (WWTP DAF skimmings). Given that sample 7 (WWTP DAF underflow) constituents are also present in sample 5, but not in sample 6, these results also demonstrate that methanogenesis is not being inhibited by the components present in the DAF underflows.

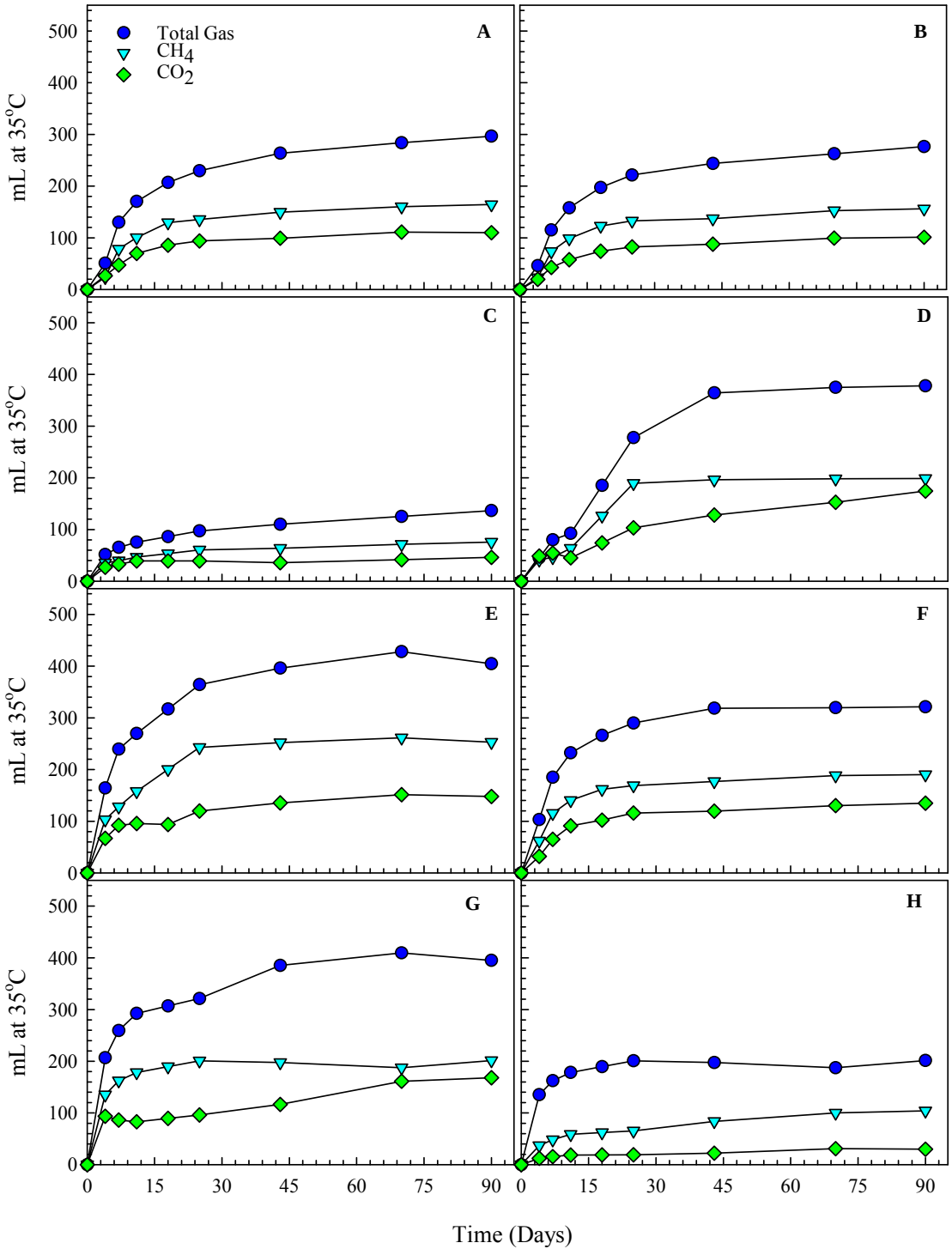

Figure 6.1. Gas production and composition of samples 1 through 8 (A through H, respectively)(Assay I; all data normalized to 1 g COD added).

6.3.1.4 Process Rates of Single Waste Samples

During the anaerobic digestion of complex organics to methane, it can be assumed that hydrolysis is the rate-limiting step and therefore the overall process rate is determined by the hydrolysis rate of the solid substrate(s). In fact, for all samples except the underflows, the soluble COD was below 5% of the total COD. Therefore, the methane production over time is an indirect way to determine the hydrolysis/process rate. In batch assays, methane generation can be described by a pseudo-first order reaction, and then the methane COD consumed over time can be expressed as:

$$COD(t) = CODtotal(1 - e^{-kt}) \qquad (6.6)$$

where $COD_{(t)}$ and COD_{total} is degradable COD at time t and ultimately, respectively (mg/L), and k is the pseudo-first order rate constant (d^{-1}). In this equation, the initial COD (COD_{total}) corresponds to the total methane-COD produced in each sample, and corresponds to a value of 100% at a relatively long incubation period. The experimental data of methane production over time (in terms of COD) were fitted to the above equation and the rate values (k ± standard deviation, d^{-1}) were obtained for each waste sample or sample combination using non-linear regression (SigmaPlot v.10). Figure 6.2 shows the fitted curves on COD consumption data for all single samples except the underflows, plus the reference series (i.e., dextrin/peptone). The rates corresponding to the manufacturing part of the system, i.e., the flotation cell samples and the mill skimmings, have similar rate values, probably because the biodegradable portion of these two samples is mostly of the same nature.

There is a large difference in the rates of the WWTP DAF influent and skimmings, the only difference in composition being that the skimmings are free from soluble substances in the influent (present in sample 7, WWTP DAF underflow). It is possible that, although the soluble components of the underflow (sample 7) do not inhibit methanogenesis, they alter the enzymatic performance of certain members of the community involved in steps prior to methanogenesis. Another factor may be that part of the biodegradable portion of the DAF skimmings is polymers used in the flotation, which might be more readily hydrolyzed and converted to methane.

Finally, given the bi-phasic nature of the data, COD consumption for WAS samples was fitted with two curves, representing a first fraction that is more easily degradable than the second fraction. There may be different processes occurring in this sample that lead to the observed results. Taken all together with the low relative specific methane production value, and observing that sulfate concentration is higher in this waste stream than in the others (except for the WWTP DAF underflow, which goes into the aeration tank and then the clarifier), with a value of 50 mg sulfate-S/L compared to around 3-30 mg/L in other samples, it seems that in this sample, sulfate reduction and methanogenesis are competing processes.

With the exception of the first phase of degradation of the WAS sample (Figure 6.2), all other waste samples had pseudo-first order rate values below 0.11 d^{-1}, which are much lower than the value of 0.19 d^{-1} for the dextrin/peptone (i.e., reference) series. The observed difference in the rate values is attributed to the fact that the dextrin/peptone sample was soluble, whereas all waste samples were of particulate nature. These results indicate that the overall process rate depends on the hydrolysis of the particulate matter.

Literature data on the kinetics of cellulosic material come from studies, which most of them were performed using pure substrates and either pure or mixed cultures. Very limited literature data exist on the hydrolysis of complex substrates, such as paper mill waste, using mixed microbial communities. Table 6.6 shows several values obtained from the literature. From these values, it can be concluded that faster degradation rates are obtained when pure cultures are fed with pure substrates in batch reactors. For complex substrates, such as newspaper, these values are much lower and more similar to the values obtained in this study. For chemostats operating with pure substrates and mixed cultures, the values are also lower than in batch systems with single species and pure substrates. The results from this study are consistent with the above observations. It is also observed that hydrolysis is the rate-limiting step which determines the overall process rate, and substrate particle size plays an important role (Pavlostathis and Giraldo-Gomez 1991; Rittmann and McCarty 2001; Song and Clarke 2009). In our study, the solid wastes generated by the manufacturing process had particle sizes on a mm scale. It is therefore reasonable to assume that hydrolysis was probably the rate-limiting step in this case.

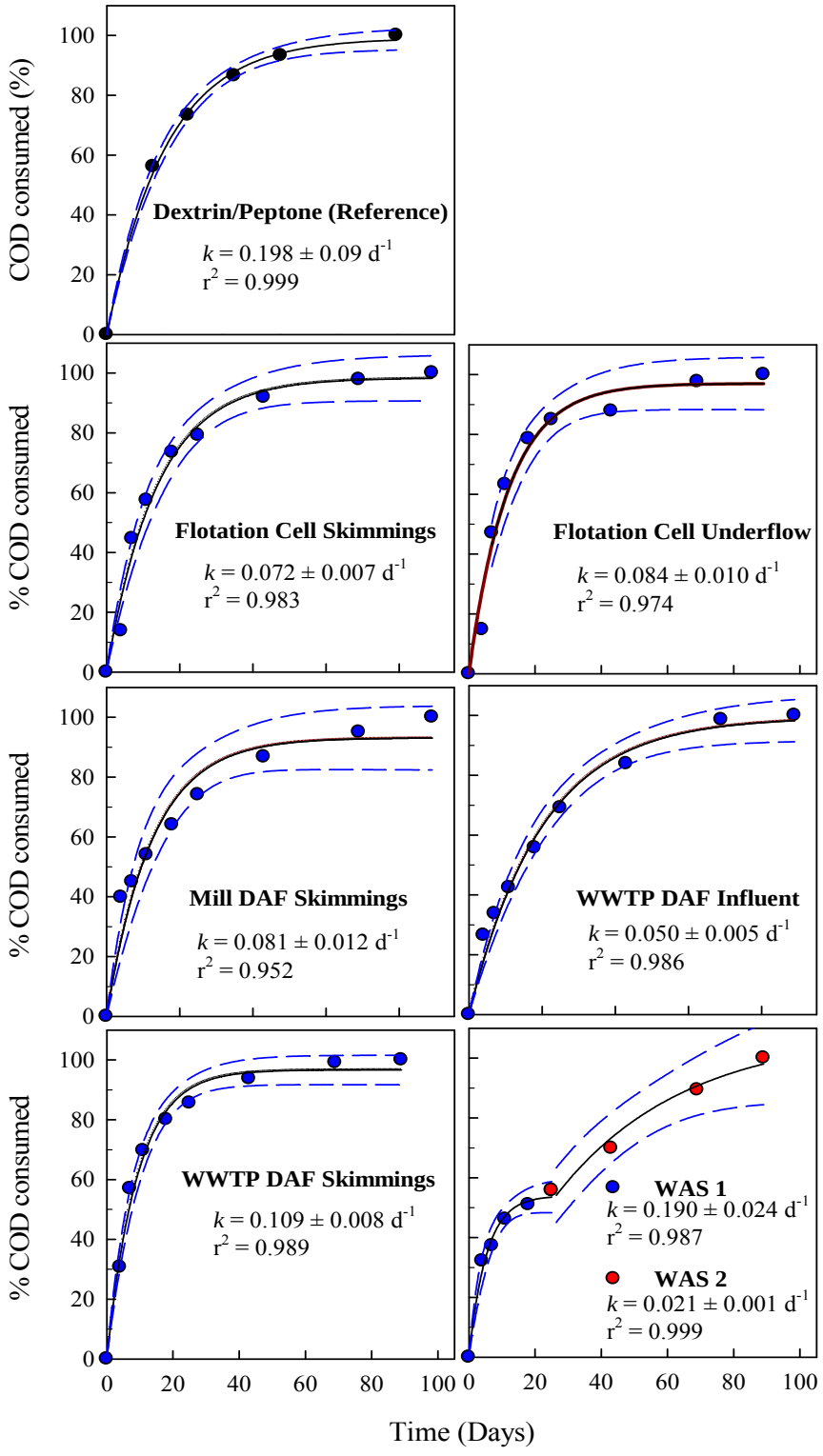

Figure 6.2. COD consumption over time for the dextrin/peptone (Reference) series and samples 1 through 8 (Assay I). Pseudo-first order rate constants (k ± standard error, days^{-1}) were obtained by curve fitting each data set. Dotted lines correspond to 95% confidence intervals.

Table 6.6. Rate constants for anaerobic degradation of cellulosic material (Literature data)

Substrate	Culture	k (d^{-1})	Reactor type
Cellulose	Pure	1.18[a]	Batch
Cellulose	Pure	0.42[a]	Batch
Cellulose	Pure	0.15[a]	Batch
45 μm Cellulose	Pure	0.74 [b]	Batch
Microcrystalline Cellulose	Mixed[e]	0.45[b]	continuous (θ = 5 d)
Cellulose powder	Mixed	0.09 [b]	Continuous
Newspaper	Mixed	0.049[c]	Not specified
Deinking sludge	Mixed[f]	0.07[d]	Batch
Paper mill sludge	Mixed[f]	0.1 [d]	Batch

[a] Pavlostathis and Giraldo-Gomez 1991
[b] Song and Clarke 2009
[c] Rittmann and Mc Carty 2001
[d] This study
[e] From leachate from yard, food and paper waste
[f] Mixed methanogenic culture fed with dextrin and peptone

6.3.2 Ultimate Biodegradability of Combined Waste Samples (Assay II)

Two sample combinations were assessed for their biodegradability in a batch assay and compared to a reference sample of dextrin and peptone. The combinations were either achieved by mixing the skimmings from the Flotation Cell and the Mill DAF, or the skimmings from the WWTP and WAS. The initial and final composition was compared, as well as the evolution of total gas, methane and carbon dioxide, in order to determine the extent of anaerobic degradation of each waste sample combination under ideal, batch conditions. The results obtained for each of these parameters are shown in Table 6.7 and discussed below.

Table 6.7 Results for ultimate biodegradability of combined waste samples (Assay II).

Parameter	Combinations			
	11	12	13	14
	WWTP DAF:WAS (0.6:1)	WWTP DAF:WAS (3:1)	WWTP DAF:WAS (6:1)	FC:Mill[a] (1:2.6)
Initial pH	7.1	7.1	7.1	7.1
Final pH	6.9	6.8	6.8	7.02
Initial total COD, mg/L	2478	2509	3144	773
Final total COD, mg/L	895	1415	1754	572
Total COD destruction,%	63.9	50	44.2	26
Initial total solids, mg/L	2414	2858	3757	456
Final total solids, mg/L	1768	2096	2825	247
Total solid destruction, %	26.8	26.6	24.8	45.9
Initial volatile solids, mg/L	1185.2	1422.6	1837.6	68
Final volatile solids, mg/L	756.3	886.8	1325.9	33
Volatile solid destruction, %	36.2	37.7	27.8	51.5
Total methane produced/g COD added, mL at 35˚C	158.1	189.3	198.8	190
CH_4, %	55.6	61.5	56.3	49.7
COD Balance	0.3	0.01	-0.05	-0.05
Relative specific methane production	0.63	1.1	1.14	1.09

[a] FC, Flotation Cell

6.4.2.1 COD Reduction and Gas Production

Both combinations (Flotation Cell and Mill DAF skimmings, and WWTP DAF and WAS) produced more methane than CO_2, as expected. Figure 6.3 shows the total gas and gas composition over the incubation time for the four combinations evaluated. From the combinations of WWTP DAF skimmings and WAS, a trend of increasing gas production was observed as the proportion of DAF skimmings increased, which was expected given that this sample produced more methane per gram of COD than the WAS. For the skimmings combination, considering the COD reduction for each single sample (Table 6.4), at a proportion of 1:2.6 the expected COD destruction was 27.9% and the measured COD destruction in the batch assay was 26%, which is in good agreement with the expected COD destruction value.

In the single sample assay, the WWTP DAF skimmings and WAS had a COD reduction of 66% and 30%, respectively. Therefore, when combined, it was expected that the values obtained for each combination would lie in this range, with differences that would depend on the proportions of each sample (43.5, 57 and 60.9%, respectively). In the cases where the skimmings were more abundant, the COD destruction was around 44%, which is lower than expected (Table 6.6). However, relative specific methane production values close to 1 were observed, and the gas composition was 60% methane and 40% carbon dioxide. No significant differences were observed between the two waste combinations tested. When WAS was the predominant component of the combination, a higher COD destruction value than the expected was obtained, 60%. However, when the relative specific methane production (0.5), as well as the gas composition are considered (50% methane and 30% carbon dioxide), the COD reduction cannot be attributed solely to

methanogenesis. Other processes are likely taking place, as was also observed when evaluating the biodegradability of the WAS alone. Finally, comparing all combinations (tests 12, 13 and 14), the ultimate amount of gas produced per gram of COD added is very similar. However, the trends in the rate of production differ (see below), which will impact the amount of gas obtained in semicontinuous flow reactors.

6.3.2.2 Solids Destruction

For the WWTP DAF and WAS combination, consistent with the single waste sample assay, none of the samples exceeded a solids destruction of 26%, which was the value obtained for WWTP DAF skimmings (Table 6.5). For the Flotation Cell and Mill DAF skimmings combination, it was expected that a solids destruction of 51% should be achieved, according to the ratio between the two waste streams. A value of 46% was obtained.

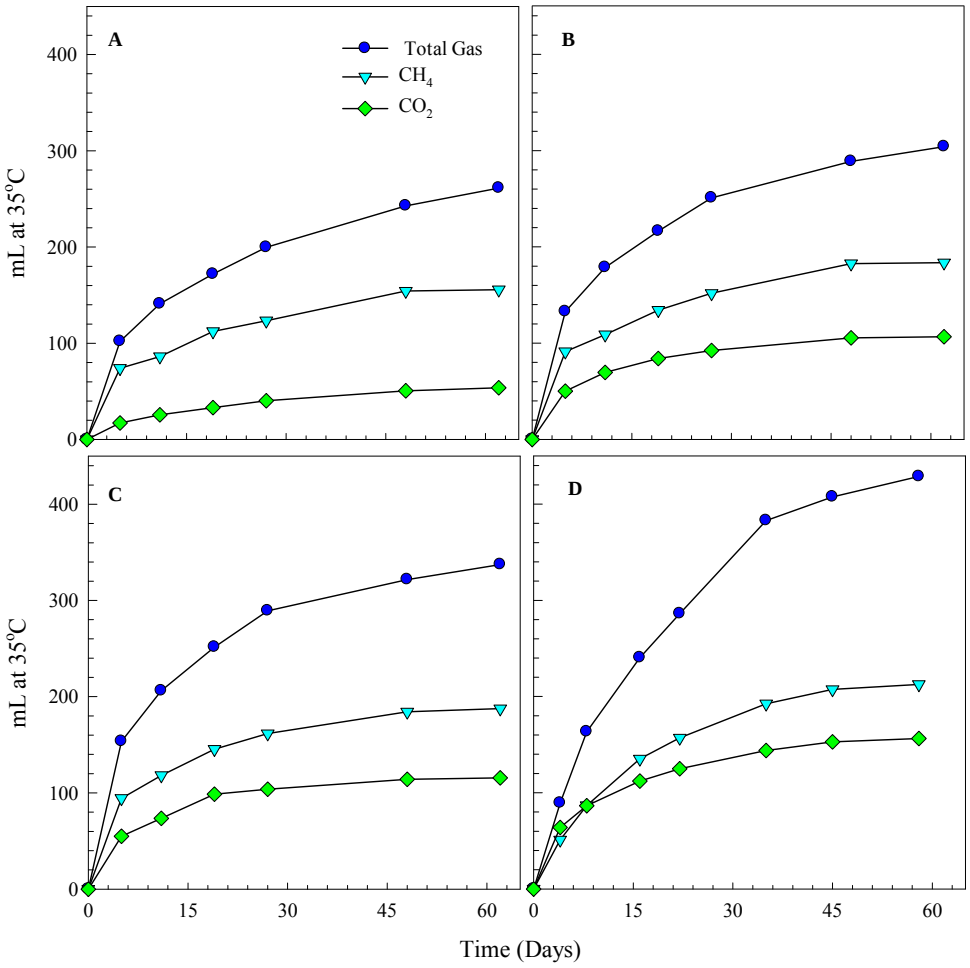

Figure 6.3. Gas production and composition of combined waste samples (Assay II). A) WWTP DAF skimmings:WAS, 0.6:1; B) WWTP DAF skimmings:WAS, 3:1; C) WWTP DAF skimmings:WAS, 6:1; D) Mill DAF skimmings:Flotation cell skimmings, 2.6:1 (All data normalized to 1 g COD added).

6.3.2.3 Process Rates of Combined Waste Samples

After obtaining values of methane production in batch assays using combined waste samples, the experimental data were fitted to equation 6.6 in order to compare the process rate of each combination, as was done with the single waste samples. Figure 6.4 shows the rates calculated for the three combinations of Flotation Cell and Mill DAF skimmings, and the WWTP DAF skimmings and WAS combination. As expected, the combination with the higher proportion of WAS had the lowest rate value, which increased directly as the proportion of DAF skimmings increased. For the Flotation Cell and Mill DAF skimmings combination (Feed 1), however, the *k* value is lower than for each of the constants for the corresponding single waste samples, but not significantly. Even though the ultimate biodegradability of Feed 1 is comparable to the WWTP DAF and WAS combinations, its rate of COD destruction is lower.

As was also observed in single waste sample assays, the rate of COD consumption of the reference sample under the same conditions used for the combined waste samples was much higher than any rate of the combined waste samples (Figure 6.4). During incubation of combined samples, organic acid production was also monitored, and compared to methane production in COD equivalents. For each waste combination, no significant organic acids levels were detected after 7 days of incubation. This observation along with the rate values obtained, suggest that, as was the case with single waste samples, the methanogenesis rate was determined by the hydrolysis rate of particulate matter.

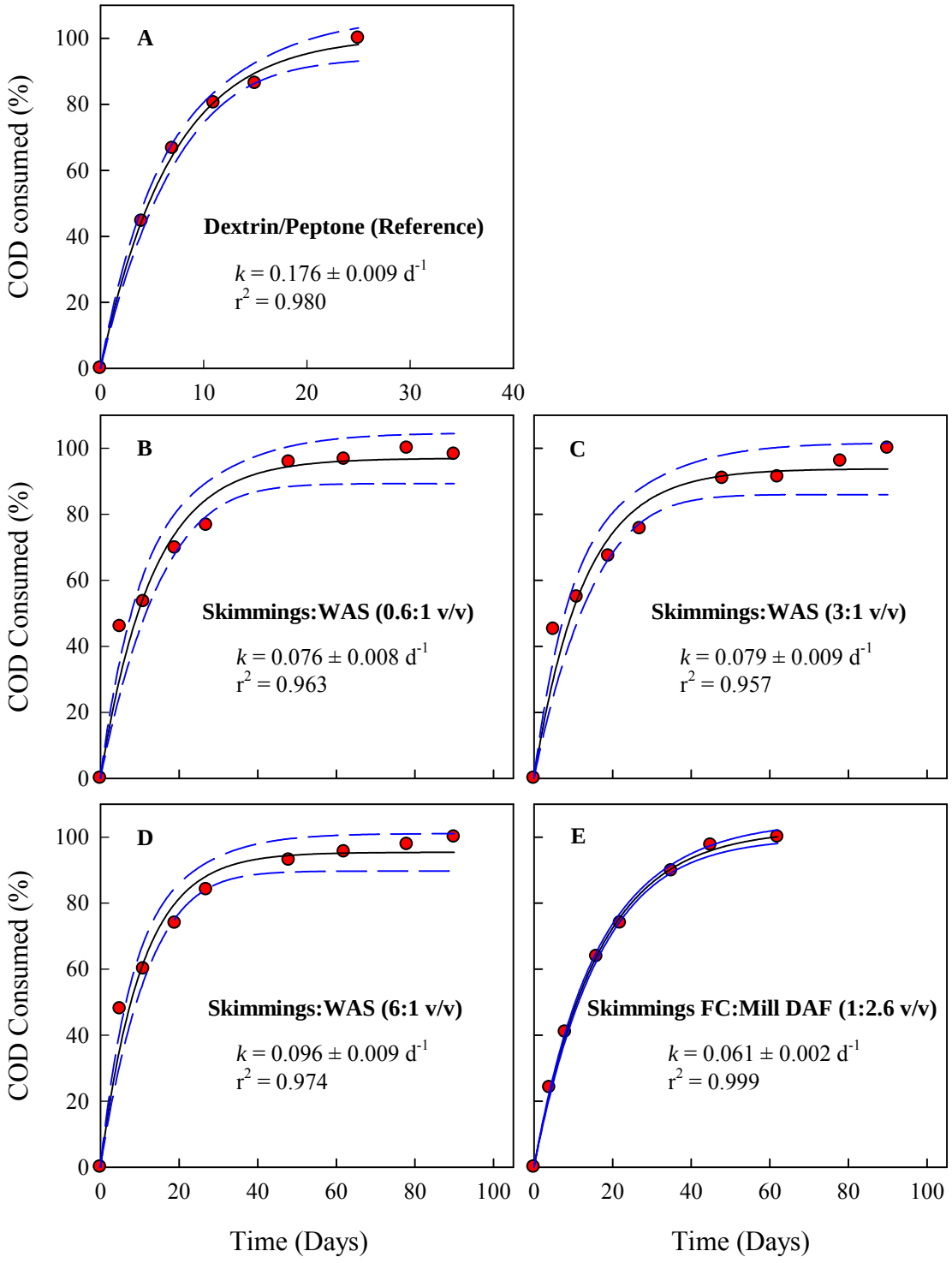

Figure 6.4. COD consumption over time for combined waste samples. Pseudo-first order rate constants (k ± standard error, days^{-1}) were obtained by curve fitting each data set. A) Dextrin/peptone (Reference); B-D) Different volumetric ratios of WWTP DAF Skimmings to WAS; E) Combination of Flotation Cell Skimmings and Mill DAF Skimmings. Dotted lines represent 95% confidence intervals.

CHAPTER 7

SEMICONTINUOUS FLOW REACTORS FOR ANAEROBIC DIGESTION

7.1 Introduction

The ultimate biodegradability of various waste streams, single and combined, was determined in batch reactors under ideal, laboratory conditions (Chapter 6). However it is also necessary to determine the extent of methanogenesis and solids destruction in continuous flow systems, which are more likely to be implemented in this kind of industry, where the volumes of water and solids generated per day are extensive. Therefore, the purpose of this phase of the study was to assess the anaerobic digestion and methane production of two selected paper mill wastewater streams in small-scale semicontinuous flow anaerobic reactors operated at different retention times. The criteria employed for the selection of the combined waste streams and their volumetric ratios included the biodegradability of the wastes (methane generated/g COD added) obtained from the batch assays (Chapter 6), as well as the infrastructure and operational conditions (e.g., volumes of wastes generated) at the study paper mill.

7.2 Materials and Methods

7.2.1 Experimental Setup

7.2.1.1 Reactor Setup and Operational Conditions

Two sets of reactors were set up in glass reactors. Each reactor had a total volume of 2.25 L and three openings: one at the top, one near the top and one near the bottom. A perforated rubber stopper with a neoprene tube was placed in the top opening to allow for gas measurements, a rubber stopper secured with an aluminum crimp on the other upper opening to allow for gas sampling and composition measurements, and a silicone tube for wasting and feeding was inserted on the lower opening and sealed via a metal clamp. Agitation was maintained with magnetic stirrers, and the reactors were kept at 35˚C throughout the experimental period. A picture of the reactors is shown in Figure 7.1.

Figure 7.1. Semicontinuous flow reactors used in this study (Four reactors were maintained at a constant temperature of 35˚C and fed with two combinations of paper mill wastes).

All reactors were started up with 1 L of the mesophilic methanogenic culture described in Chapter 4. After flushing each reactor with helium gas for 5 minutes, 950 ml of the methanogenic culture (3 g VS/L) and 50 ml of anaerobic culture media were added. Wasting and feeding of the reactors were done by transferring the liquids with a 60 mL syringe through the lower opening. Table 7.1 shows a summary of the experimental setup for this phase of the study, and a summary of the reactors' operating conditions is shown in Table 7.2.

Table 7.1. Start up conditions of the semicontinuous flow reactors used in this study.

Parameter	Value
Total Volume, mL	2250
Working Volume, mL	1000
Head Space, mL	1250
Methanogenic Culture Volume, mL	950
Culture Media, mL	50

Table 7.2. Operational conditions of the semicontinuous flow reactors used in this study.

Parameter	Experimental Period	Reactor 1	Reactor 2	Reactor 3	Reactor 4
Feed type		Feed 1 FC + Mill DAF skimmings	Feed 2 WAS + DAF skimmings	Feed 1 FC + Mill DAF skimmings	Feed 2 WAS + DAF skimmings
SRT (days)	1	30	30	20	20
	2	20	20	15	15
	3	7	7	15	15
Feed rate (mg COD/day)	1	309	782	515	1,304
	2	515	1304	690	1,747
	3	1,472	3,729	690	1,747

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This phase of the study was conducted in three experimental periods (Table 7.2), of which only three allowed the reactors to reach steady state. All semicontinuous flow reactors were operated for 100 days for four different retention times. Initially, two sets of reactors (with Feed 1 and Feed 2) were operated at SRTs of 30 and 20 days (period 1). Before the completion of the first retention time (i.e., on day 17), the SRT values of the reactors were changed to 20 and 15 days, respectively (period 2). Finally, the SRT of the two reactors operated at a SRT of 20 days in period 2 were reduced to 7 days (period 3) on day 89. The composition of Feed 1 was changed on day 18, from a feed composed of the WWTP influent only, to a mixture of the flotation cell skimmings and the mill DAFs skimmings. This change was necessary after considering that treating the skimmings alone (i.e., the most concentrated waste streams), would be more appropriate for anaerobic digestion systems.

7.2.1.2 Culture and Samples

The same mixed, methanogenic culture used in the batch assays, obtained from a culture maintained in the laboratory, was used in this phase of the study. Details for this culture were described in Chapter 3. The selected waste streams consisted of a combination of the skimmings from the deinking flotation cells and the mill DAF (FC:DAF, 1:2.6 v/v; Feed 1), and a combination of the wastewater treatment plant DAF skimmings and WAS (DAF:WAS, 3:1 v/v; Feed 2).

7.2.1.3 Monitoring

Reactor wasting and feeding was initially practiced every day and the excess gas produced was measured and released every 5 days. However, starting on day 50, both wasting and feeding as well as gas measurement were performed every 2 days. Gas composition was also measured frequently, initially every 5th day and later more often. Nutrients, specifically nitrogen as ammonia and phosphorus as phosphate, were measured at least once a week, and the pH was monitored initially every 5th day and later twice a week, according to the methods described in Chapter 4.

7.2.1.4 Modifications to the System

Nitrogen and phosphorus are the most important components of biomass after carbon, oxygen, and hydrogen. As the waste used in our study had only trace levels or none at all of nitrogen and phosphorus, it was expected that these nutrients would need to be supplemented. However, in methanogenic systems, the nutrient requirements are expected to be lower than those for aerobic systems. For this reason, nitrogen and phosphorus were monitored periodically to avoid any nutrient limitation for anaerobic microbial growth evidenced by a drastic decline in gas production. For practical purposes, a lower concentration limit was set at 20 mg/L of NH_4-N and 10 mg/L of PO_4-P. Another consideration was to add both N and P but at a minimum amount necessary to keep the treatment costs low. Nitrogen was added as ammonium chloride (NH_4Cl) and phosphorus as potassium phosphate ($K_2HPO_4^{3-}$). Nutrients were added to both feeds to ensure equal concentration of ions in all reactors. Finally, the pH of every reactor was monitored to avoid the reactors' pH dropping below 6.5.

7.3 Results and Discussion

7.3.1 Flotation Cell Skimmings and Mill DAF Skimmings Combination (Feed 1)

Two periods of stability were observed for Feed 1 reactors as shown in Figure 7.2A. Stability was initially achieved after 10 days of operation, and continued to day 49. A second period was observed from day 54 to day 88 for Reactor 1, which occurred upon change of the feed. The change in SRT from 30 to 20 days was done on day 17, but as it can be seen in Figure 7.2A, gas generation remained constant. For the 30/20 day SRT, the gas produced in each steady period was 84 and 146 mL/day, and for the 15 days SRT, it was 103 and 132 mL/day. The second stability period resulted in a higher total gas production (and therefore methane production) with a significant increase of the methane content to around 50%. The methane content was 45 and 48% at an SRT of 20 and 15 days (Reactor 1 and 3, respectively) during both stability periods. Finally, after the establishment of a 7 day SRT at day 88, 178 mL/day were produced, on average with Feed 1. COD destruction was considered only on the last stable period. At a SRT of 20, 15 days, and 7 days, 27, 22, and 11% COD reduction was achieved (Table 7.3), with a relative specific methane production close to 1. As expected, total and volatile solids destruction for the three SRTs were less than that achieved in the batch assays performed over 90 days (see Chapter 6). The solids destruction was expected to be below 45.9% and the values obtained were 33.6, 30.5, and 15% for SRTs of 20, 15 and 7 days, respectively. The volatile solids destruction was normalized to the biodegradable portion only, and the percentage destruction was then calculated as:

$$Normalized\ VS\ destruction\ (\%) = \frac{Reactor\ VS\ destruction\ (\%)}{Ultimate\ VS\ destruction\ (\%)} x100 \qquad (7.1)$$

Therefore, considering only the biodegradable portion, a range of 85% to 30% VS reduction was achieved at the three retention times (Table 7.3).

With respect to the operational conditions, as it is shown in Figure 7.2, when the reactors were fed without any amendment, the pH dropped by one unit in the period of one solids retention time for both reactors 1 and 3. Bicarbonate alkalinity was supplemented to both reactors at 2.36 g $NaHCO_3$/L, which stabilized the pH at/or above 6.7 throughout the rest of the operating period, until the SRT was changed to 7 days. In the last period, even though the feed was amended with the same amount of bicarbonate, the pH dropped to around 6.4. However, for this feed, even at pH values of 6.4, the reactors were stable, and gas production was equal to that achieved at higher pH values (Figures 7.2B and 7.2C).

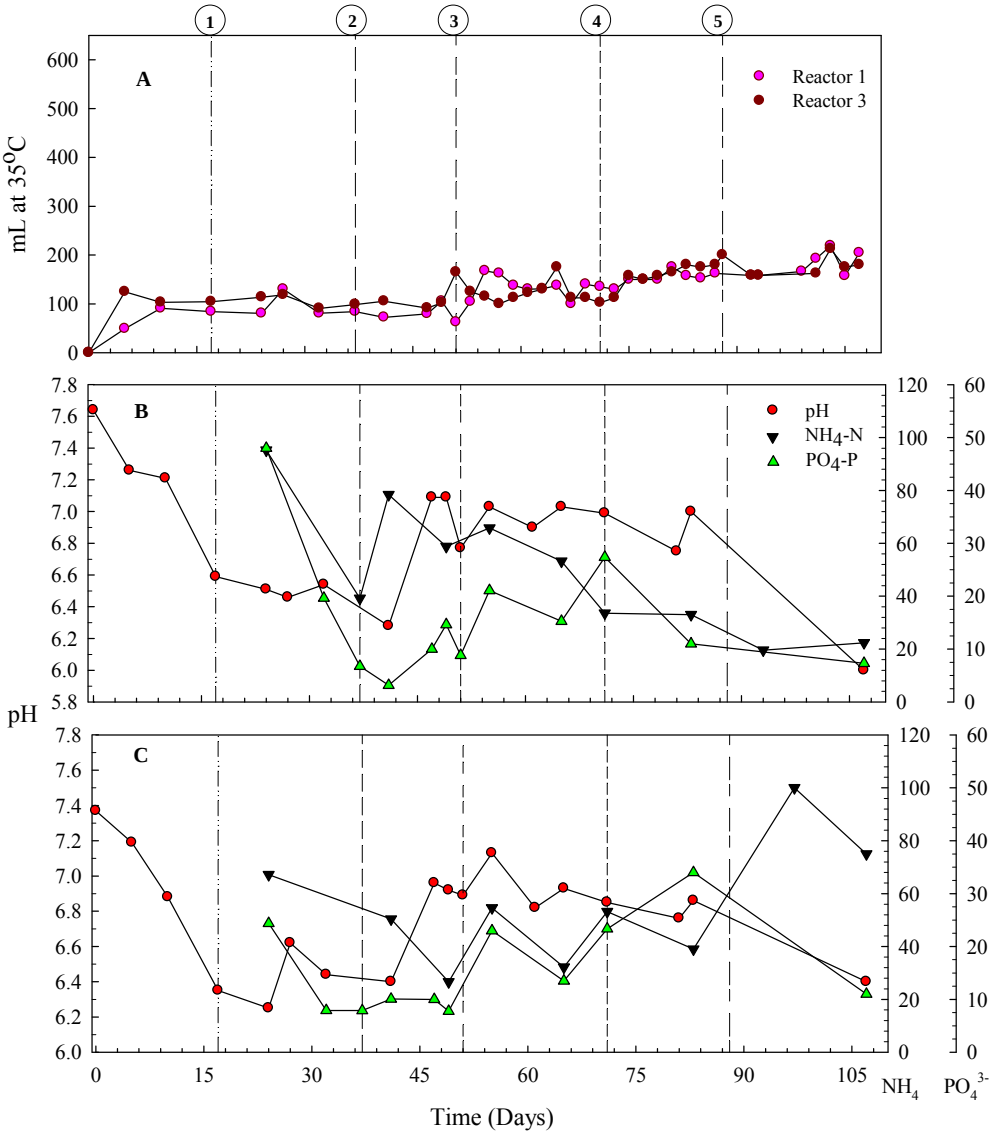

Figure 7.2. Total gas production (A), nutrients and pH (B & C) of reactors operated with Feed 1. A) Total gas production by Reactor 1 and 3 (SRT 20/7 and 15 days, respectively); B and C) Nitrogen, phosphorus, and pH variation in Reactor 1 and 3, respectively. Dashed lines: 1) Change of SRT from 30 to 20 and from 20 to 15 days; 2) Initial amendment of nutrients and bicarbonate; 3) Additional amendment of phosphorus; 4) Increased ammonia concentration in the feed; 5) Change of SRT in Reactor 1 from 20 to 7 days.

Table7.3. Reactors' performance during the stable operation period (Reactor 1 and 3; Feed 1).

Parameter	SRT, days		
	20	15	7
TS in, mg/day	770±1[c]	1089±2	2509±20
TS out, mg/day	513.4±14	743±21	2145±6
TS reduction (%)	33.3	32.0	15
VS in, mg/day	590±28	791±37	1151±54
VS out, mg/day	238±10	373±1	1226±14
VS reduction (%)	59.5	52.8	19
Normalized VS reduction (%)[a]	84.9	75.3	27
COD in, mg/day	515±25	690±34	1991±68
COD out, mg/day	376±15	536±27	1780±161
COD reduction (%)	27.0	22.3	11
CH_4 mL at 35°C/g COD added	122.2	93.7	43
COD Balance[b]	0.0	0.0	0.0
Relative SMP	1.1	1.1	1

[a] Normalized to the biodegradable portion of VS (obtained in Batch Assay II).

[b] Obtained using equation 6.2 (Chapter 6)

[c] Mean ± standard deviation ($n \geq 5$)

Monitoring of ammonia indicated that at day 37, no ammonia was detected in Reactor 3 effluent. It was therefore supplemented with 65 mg/L of NH_4-N added directly to the feed. As a result, 50% increase in gas production was observed after ammonia supplementation which led to the second stable period (Figure 7.2A). At day 77, as gas production started to decrease in Reactors 2 and 4 fed with Feed 2 and ammonia levels were decreasing, the nitrogen concentration was increased in Feed 1 to 100 mg NH_4-N/L, to maintain the same cation concentration in both feeds, which resulted in a COD:N ratio

of 100:1. At day 95, 100 mg/L of ammonia was introduced in Reactor 3 (SRT of 15 days).

With respect to phosphorus, it was also observed that without any amendment, its concentration dropped to 3 mg PO_4^{3-}-P/L and was not detected in Reactor 3 (SRT 15 days) at day 47. After an initial addition of 10 mg PO_4^{3-}-P/L directly to all reactors, both feeds were amended equally at the same phosphorus concentration. However, after 10 days of operation (day 55), its value decreased again to 2 mg P/L in Reactor 4. As a result, 20 mg phosphate-P/L was added to all four reactors and the two feeds. From this point onwards, the phosphate-P concentration in all reactors effluents was at/or above 13 mg P/L at all times. The final COD:P ratio was 100:0.13. As with ammonia, amendment of phosphorus coincided with an increase in gas production. This final nitrogen and phosphorus concentration in the feed remained as such until the end of the incubation period. The reactors operated at a SRT of 7 days were therefore fed with a COD:N:P ratio of 100:1:0.13.

7.3.2 WWTP DAF Skimmings and WAS Combination (Feed 2)

From the Feed 2 reactors (Reactor 2 and 4), only one final stable period was achieved in Reactor 4, from day 71 onwards, which occurred after increasing the alkalinity in the system and supplementing the feed with both nitrogen and phosphorus. Figure 7.3 A shows the gas production throughout the incubation period for Reactors 2 and 4 (SRTs 20/7 and 15 days, respectively). For Reactor 2 operating at a 20 days retention time, a stable period was achieved at day 71, and also after changing its SRT to 7 days. For the

stable period, the total gas produced was on average 280 and 389 ml/day for SRTs of 20 and 15 days, respectively, and the gas methane content was 55%. At day 89, when the SRT of 7 days was established, the total gas produced was, on average, 450 mL/day.

The COD reduction was 42, 34, and 22%, at SRTs of 20, 15, and 7 days, respectively. These values are consistent with the results of the batch assay, where the ultimate biodegradability for these combined samples was 44% (Table 6.6). The relative SMP value ranged from 0.7 to 1 (Table 7.4).

Figures 7.3B and 7.3C show the reactors N and P, as well as pH values for the entire experimental period. Before the end of the first retention time with Feed 2, nutrients dropped to non detectable levels in Reactor 4 (SRT 15 days). However, gas production was not severely affected, although it did not stabilize. On day 47, 65 mg/L NH_4-N was added directly to the reactors and to the feeds resulting in a final feed concentration of 50 mg NH_4-N/L. After the ammonia-N amendment, gas production increased. However, on day 65, the gas production started to drop again. Ammonia data indicated that even though 50 mg N/L was added to the feed, it was being consumed. As a result, the concentration of nitrogen in the feed was raised to 100 mg N/L, resulting in a final COD:N ratio of 100:0.5. This concentration of nitrogen allowed the reactors to remain stable since day 71 onwards. Ammonia was supplemented to Reactors 3 and 4 (SRT 15 days), because, even though gas production was maintained, the level dropped to below 20 mg/L. Ammonia was not added the Reactors 1 and 2, operated at 7 days retention time.

Phosphate-P was monitored in all reactors and supplemented as mentioned above on day 47, after a drop from 1.4 mg P/L at day 40, to non detectable levels at day 47. In spite of the P supplementation at 10 mg P/L, only 1.3 mg P/L were detected after 5 days. As a result, 20 mg P/L were added to the reactors and to the two feeds and maintained at this level until the end of the study, resulting in a final COD:P ratio of 100:0.08.

As shown in Figure 7.3B and C, and discussed above, within the first SRT the pH dropped below 6.5. Sodium bicarbonate was added to all reactors and to the media on day 47, and since then the pH never dropped below 6.7, until the 7 day retention time period, where the pH dropped to around 6.4. However, the pH decline did not affect the gas production rate.

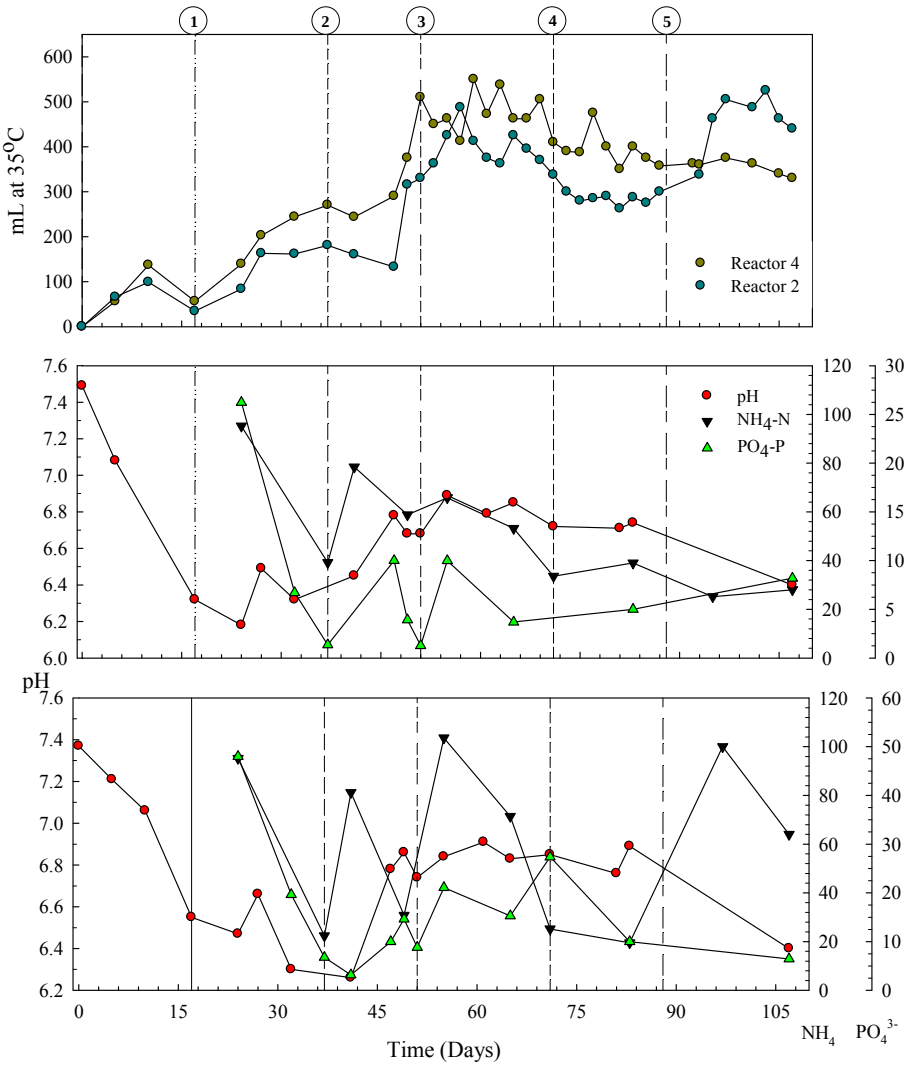

Figure 7.3. Total gas production (A), nutrients and pH (B & C) of reactors operated with Feed 2. A) Total gas production by Reactor 2 and 4 (SRT 20/7 and 15 days, respectively); B and C) Nitrogen, phosphorus, and pH variation in Reactor 2 and 4, respectively. Dashed lines: 1) Change of SRT from 30 to 20 and from 20 to 15 days; 2) Initial amendment of nutrients and bicarbonate; 3) Additional amendment of phosphorus; 4) Increased ammonia concentration in the feed; 5) Change of SRT in Reactor 2 from 20 to 7 days.

Table7.4. Reactors' performance during the stable operation period (Reactors 2 and 4; Feed 2).

Parameter	SRT, days		
	20	15	7
TS in, mg/day	1428±5[c]	1914±8	3764±130
TS out, mg/day	1297±12	1730±4.5	3286±7
TS reduction (%)	9.2	9.6	13
VS in, mg/day	703	942	1818±58
VS out, mg/day	456±1	609	1075±14
VS reduction (%)	35.1	35.3	41
Corrected VS reduction (%)[a]	93.5	84.9	108
COD in, mg/day	1304±86	1747±116	2024±33
COD out mg/day	749±48	1144±81	1578±12
COD reduction (%)	42.5	34.5	22
CH_4 mL at 35^{o}C/g COD added	118.1	119.6	122
COD Balance[b]	0.1	0.0	0
Relative SMP	0.7	0.9	1

[a] Normalized to the biodegradable portion of VS (obtained in batch Assay II).

[b] Obtained using equation 6.2 (Chapter 6)

[c] Mean ± standard deviation ($n \geq 5$)

7.3.3 Feed 1 vs. Feed 2

For Feed 1 reactors, the second stability period resulted in a higher total gas (and methane) production with a significant increase of the methane content to around 50%. However, the final gas production of about 150 ml/day is almost 3 times less than that achieved with Feed 2 reactors, as the Feed 2 COD loading was higher as well as more degradable (around 25% for Feed 1 and 35% for Feed 2 on a COD basis). The volume of methane produced per gram of COD added to each reactor was similar: 117 mL for Feed 1 and 172 mL for Feed 2 at a SRT of 7 days, respectively. Chemostats operated at 5 days SRT and fed with 1,900 mg COD/L with similar biodegradable cellulosic material (around 50%) produced 165 mL of methane per gram of COD added, a similar value to the ones found in the present study (Song and Clarke 2009).

Initially, the two feeds were not amended, but in both cases nutrients had to be supplemented in order to avoid any nutrient limitations (N and P). The nutrient limitations had a larger influence on gas production in reactors operated with Feed 2, which is more degradable than Feed 1. Feed 1reactors were not affected as much by the low availability of N and P, because their degradable COD loading was lower than that of the reactors fed with Feed 2. The gas production of Feed 2 reactors was only stabilized when a COD:N:P of 100:0.5:0.08 was achieved.

It was observed that, even though the pH decreased with time at the initial operating period (period 1), the total gas production did not change for Feed 1reactors. However, only after the addition of alkalinity, the total gas production stabilized in Feed 2 reactors. A recent study conducted by Taconi et al. (2008), in which municipal solid waste was

treated in a continuous system at low pH (pH range of 4 to 7), also showed that the treatment was effective, methane was produced, but the gas production rate fluctuated.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

Solid wastes generated by the paper manufacturing industry are usually disposed of in landfills, which adds to costs that are bound to increase. Anaerobic digestion of select waste streams is a potentially applicable technology to reduce solids, decrease costs, and generate methane (revalorize the waste). Therefore, in this work, single waste streams from the manufacturing process and its wastewater treatment of a paper producing plant in Central America, were assessed in order to determine the ultimate biodegradability and the potential of combined waste samples to be digested anaerobically. Overall, anaerobic digestion appears to be feasible for this type of wastes. For single samples, the volatile solids reduction ranged from 25 up to 85%, corresponding to WAS and Flotation Cell Skimmings, respectively, and when two waste stream combinations were tested in semicontinuous flow digesters, the volatile solids reduction was 55 and around 31% for Feed 1 and Feed 2, respectively. The methane production was about 120 ml of methane per gram of COD added for both feeds (at 35^{o}C and 1 atm.) with a SRT above 15 days.

From this study, several specific conclusions were obtained:

1) Single waste samples generated during the paper manufacturing process had a higher solids biodegradability than those generated in the wastewater treatment process. The single samples from the Flotation Cell and Mill DAF skimmings (components of Feed 1) were the two most biodegradable samples in terms of total and volatile solids destruction (75 and 42% for total, and 85 and 59% for

volatile solids, respectively). Combined, these two waste streams resulted in a greater solids destruction (total solids destruction of 52% in batch, and 15 to 33% in semicontinuous flow reactors operated at 7 to 20 days retention time, respectively). In contrast, the WWTP DAF skimmings and WAS combination (Feed 2) had 26 and 10% of total solids destruction in batch and semicontinuous reactors (in all cases), respectively.

2) Both feeds produced similar levels of methane per gram of COD added, at SRTs of 15 and 20 days, but a significant difference was evidenced at a SRT of 7 days. This is probably due to a difference in the rate of methane production. In fact, WWTP DAF skimmings had the highest (0.11 d^{-1}), as well as the initial period of WAS digestion (0.18 d^{-1}, comparable to the dextrin/peptone, i.e. reference). In the case of combined waste streams, the difference was also evidenced (0.06 vs. 0.08 d^{-1} for Feed 1 and 2, respectively).
3) There was also a very high difference in the process rate of all waste samples compared to the reference (i.e., dextrin/peptone), indicating that the methane production rate depends on the hydrolysis rate of the particulate substrate. This aspect should be further evaluated in a future study. In order to improve the overall process rate, the hydrolysis rate of the wastes prior to anaerobic digestion should be improved. There are several methods which could be used to improve the hydrolysis of lignocellulosic material, but one that may be compatible with the biological process is acid hydrolysis using acetate to lower the pH and the use of ammonia to raise it back. Acetate would then be used as a carbon source by the microorganisms and ammonia taken up as a nutrient. It should be determined

whether this method would greatly increase the overall cost, but also corrode the system in the long run, as expected.

4) In terms of reactor operation, there is no significant difference in operating at a SRT of 30 or 20 days. The system was also stable at a SRT of 7 days, although achieving a lower performance in terms of the extent of solids and COD destruction.
5) The digesters performance was greatly affected by nutrient availability, particularly nitrogen. A ratio of COD:N of at least 100:0.5 and a ratio of COD:P of at least 100:0.08 are recommended, which results in stable reactor performance with maximum methane production.
6) In terms of pH, both feeds require a significant amount of bicarbonate addition to prevent a decrease in reactor pH below 6.8 (2.4 g $NaHCO_3$/L was used in the present study). However, it was observed that Feed 1 reactors were not affected by low pH (pH = 6.4). Feed 2 reactors were not stable, but, when the pH decreased, gas production was maintained in a range higher than that achieved during the first days of operation. Therefore, alkalinity addition and pH control would be necessary, but should not be a primary concern for the reactor performance.
7) Paper manufacturing generates effluents that are already at the desired temperature range for methanogenesis (initially at 60˚C, lowered to around 40˚C after waste mixing and heat losses are accounted for). Therefore, no extra energy is needed to support a mesophilic digestion process. For the plant considered in the present study, and others in Latin America and the Caribbean, the

implementation of mesophilic anaerobic digestion will not add significantly to the cost relative to maintaining the appropriate temperature conditions.

A comparison of methane production and the amount of energy currently used at the study paper mill was conducted using data from the plant operations. For the case of the WWTP DAF skimmings and WAS combination (Feed 2), about 600 m^3 of such waste is produced per day. Considering that the volumetric methane to feed ratio for the reactor fed with Feed 2 and operated at 15 days retention time was 3.2, assuming that all this waste was subjected to anaerobic digestion, the expected methane production at 35^oC and 1 atm would be 1,900 m^3/day. Based on the calorific value of methane (35,260 kJ/m^3 at 1 atm and 35˚C), the methane energy generated will be equal to about 6.3 x 10^7 BTU per day. Since 7.1 x 10^6 BTUs are spent per dry ton of paper produced, and 57 tons of paper are produced each day, then about 4 x 10^8 BTUs are used daily by the paper drying process. Therefore, the methane energy potentially obtained corresponds to about 15% of the daily energy used for paper drying. This is not trivial considering that the heating cost at the study plant is around $9 to $25 per million BTUs, resulting in average costs of $100,000 to $125,000 per month, depending on the use of either “bunker” or diesel oil. If 15% of the heating energy was to come from methane generated by the anaerobic digestion of Feed 2, it could result in savings of at least $200,000 per year. Added to this are savings from solids disposal fees avoided, which amounts to 10% of the $20,000 spent per month (if an improvement in dewatering is not considered), which results in cost savings of $24,000 a year. Considering the savings through both methane generation and avoidance of disposal fees, a total of about $225,000 per year could be saved. In a

similar calculation, considering that the combined flow rate of the Flotation Cell and Mill DAF skimmings (Feed 1) is about 680 m^3 per day, and the volumetric methane to feed ratio for the reactor fed with Feed 1 and operated at 15 days retention time was 1.0, the methane potentially generated would amount to $2.1x10^7$ BTUs per day, which corresponds to annual savings of $63,000. When the landfill fees are considered, a total of $90,000 per year would be saved. Considering that both oil prices and disposal fees will be higher in the future, savings will also increase. Costs associated with the construction and operation of a digestion system, as well as the addition of nutrients (nitrogen and phosphorus) and alkalinity to maintain the pH at desired levels, which are all necessary given the characteristics of the waste, should be considered. However, digester effluent returned to the aerobic biological process (e.g., activated sludge) will result in nutrients recycle, which will offset the cost for nutrients currently used for the aerobic process.

Given that the paper manufacturing operations produce the least amount of solids, it would be appropriate to evaluate the combination of these waste streams with WAS, in the case that the plant was modified in order to avoid these skimmings from re-entering the WWTP, as is currently the practice. It would also be appropriate to evaluate the WWTP DAF solids removal efficiency once the skimmings are reduced, especially in terms of inorganics. Since the nature and composition of the solids will change, it could be determined whether this is an added benefit of the anaerobic digestion process. Furthermore, it should be considered that if the skimmings generated in the paper manufacturing operations were to be anaerobically digested and therefore diverted from

the WWTP, the WWTP DAF unit may no longer be necessary. This may translate into significant cost and energy savings.

For the paper plant considered in this study, anaerobic digestion of DAF skimmings and other waste streams could potentially result in the production of over 2,600 m^3 of methane per day. From an environmental point of view, methane production in an engineered system prior to landfilling is a clear benefit since impact via uncontrolled methane release on global warming is prevented. Lastly, the degradation of toxic compounds that might leach into the soil associated with land disposal needs to be evaluated as well. This would be another benefit of implementing biological anaerobic treatment to solids prior to disposal.

Overall, methane production from the wastes generated in the paper manufacturing process is promising, but a more thorough costs/benefit analysis needs to be carried out. From the environmental standpoint, the capture of a potent greenhouse gas that is likely generated and released in uncontrolled landfills, and the reduction of the volume of solids requiring disposal, along with the beneficial use of the methane in the paper plant to cover a substantial fraction of its current energy consumption, are examples of the benefits of anaerobic digestion.

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